Washington State Toxics Monitoring Program

Monitoring with SPMDs for PBTs in Washington Waters in 2009

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For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

Washington State Department of Ecology - www.ecy.wa.gov/

Headquarters, Olympia	(360) 407-6000
Northwest Regional Office, Bellevue	(425) 649-7000
Southwest Regional Office, Olympia	(360) 407-6300
Central Regional Office, Yakima	(509) 575-2490
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Monitoring with SPMDs for PBTs in Washington Waters in 2009

by

Patti Sandvik and Keith Seiders

Toxics Studies Unit
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

Waterbody Numbers

Lower Columbia River near Clatskanie	WA-CR-1010
Middle Columbia at McNary Dam	WA-CR-1026
Upper Columbia River at Rock Island Dam	WA-CR-1040
Lake Washington	WA-08-9340
Queets River	WA-21-1030
Spokane River	WA-54-1020
Spokane River	WA-57-1010
Walla Walla River	WA-32-1010
Yakima River	WA-37-1010

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Abstract

The Washington State Department of Ecology uses semi-permeable membrane devices (SPMDs) to estimate levels of persistent, bioaccumulative, and toxic (PBT) chemicals in selected waterbodies.

This project began in 2007 with the goal to detect trends in PBT chemicals after a minimum of four years of sampling. Target chemicals included chlorinated pesticides (CPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs).

Results in this report are reported in two parts:

- Part 1: Results from the monitoring of eight sites in 2009.
- Part 2: Results from additional quality control sampling that was done to better characterize contamination and variability within the sampling system.

SPMDs were deployed for 30 days during the spring and fall of 2009. PCBs, CPs, and PAHs were detected in all samples, and PBDEs were detected in 89% of the samples. Many results were similar to 2007 and 2008 results. Highest concentrations were found in the Walla Walla, Lower Columbia, Yakima, and Spokane Rivers and Lake Washington.

Quality control sampling conducted during the spring of 2009 helped characterize contamination in the sampling system for PBDEs, PCBs, and PAHs. The ability to measure spatial or temporal trends with SPMDs at many sites appears to be compromised because levels of several target analytes at some sites are low relative to the noise[1] in the sampling system.

Recommendations include:

- Refining monitoring goals to site-specific needs.
- Discontinuing analyses for PAHs.
- Improving various quality control practices.
- Suspending sampling efforts after 2011 to reserve time to better review all results and progress towards project goals.

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[1] Background noise is the sum of all interference in a measurement which is independent of the data signal or true result found in the field sample.

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- Site access:
  - Walla Walla River: Larry and Barbara Pierce.
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  - Spokane River at Nine Mile Dam: Jeff Turner, manager.
  - Spokane River near the Idaho border: Steve Kunas, Parkwood Business Properties.
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  - Formatting and editing the final report: Joan Le Tourneau, Cindy Cook, and Gayla Lord.

PART 1: RESULTS FROM SITE MONITORING

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Introduction

Background

In 2000, the Washington State Department of Ecology (Ecology) developed a strategy to reduce persistent, bioaccumulative, and toxic (PBT) chemicals. The initiative targets chemicals that degrade slowly, tend to build up in tissues, and can have adverse health effects on humans, fish, and wildlife. A total of 27 substances are on the PBT list at this time (Appendix A). Information about Ecology's PBT initiative can be found at www.ecy.wa.gov/programs/swfa/pbt/.

To investigate the occurrences and concentrations of toxic chemicals in the state's waterbodies, Ecology began the Washington State Toxics Monitoring Program (WSTMP) in 2000. One objective of the WSTMP was to conduct trend monitoring for PBT chemicals in fish and surface water. Johnson (2007a) developed a Quality Assurance (QA) Project Plan for monitoring organic chemicals in surface water, and sampling began in 2007 for this PBT Trends Study. Target analytes included chlorinated pesticides (CPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). In 2008, polycyclic aromatic hydrocarbons (PAHs) were added to the program. Information about the WSTMP can be found at www.ecy.wa.gov/programs/eap/toxics/wstmp.htm.

Monitoring for the PBT Trends Study involves a minimum of four years of sampling twice a year at waterbodies throughout Washington State. In 2007 and 2008, 12 sites were sampled: 11 major rivers and one large urban lake. Eight rivers sites and one lake were sampled in the spring of 2009. Sampling was suspended in the fall to assess data quality issues except for one site, which was part of another study.

Standardized passive samplers called semi-permeable membrane devices (SPMDs) are used in this program to concentrate and quantify chemicals over time. The ability of SPMDs to detect low concentrations of bioaccumulative chemicals was documented from the results of the first two sampling years. Those results were published (Sandvik, 2009b; 2010b) as part of the PBT Trends Study.

Although passive samplers can reduce the variability associated with measuring concentrations in conventional water and biological samples, contamination in the sampling system threatened to compromise the usefulness of results. Corrective actions were taken, and additional quality control (QC) measures were implemented in 2009 to help define sampling and laboratory variability.

An abbreviated QA Project Plan was developed for the spring sampling in 2009 (Sandvik et al., 2009) to guide development of standard operating procedures (SOPs) for processing, reporting, and better characterizing contamination of, and variability with, SPMD data. Results were also used to update the project plan for this long-term trends monitoring project (Sandvik, 2010a).

Monitoring Design

Monitoring Sites

Figure 1 shows locations of the sampling sites for the 2009 PBT Trends Study.

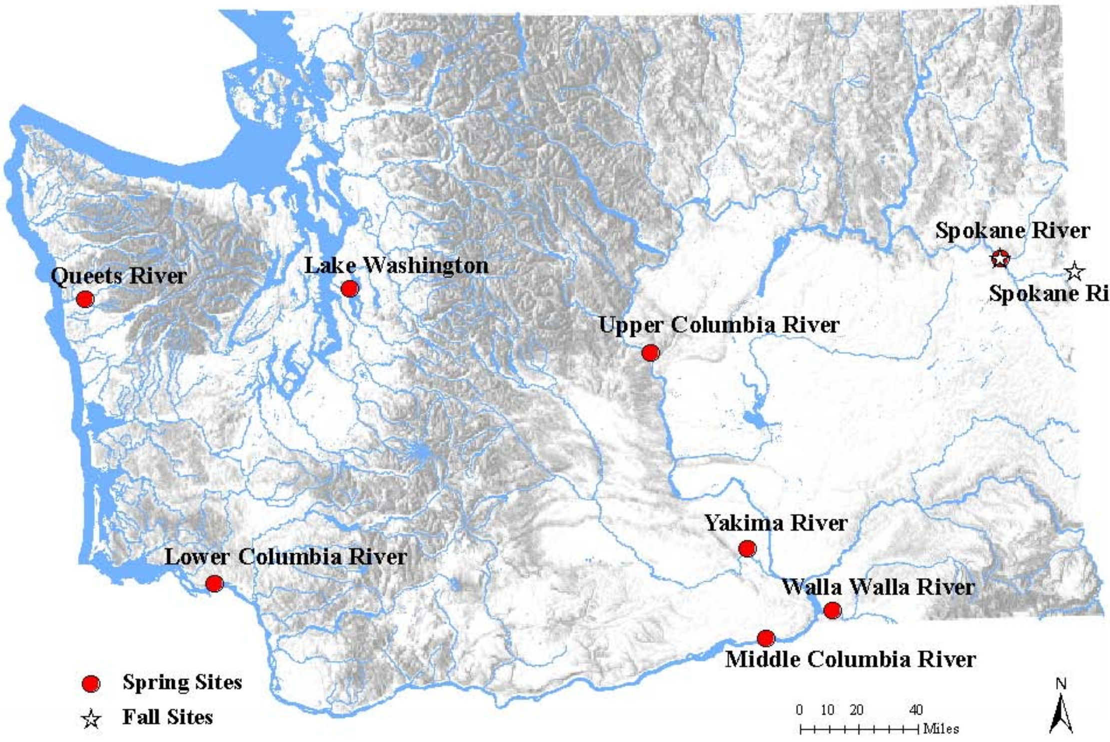

Figure 1. PBT Trends Monitoring Sites in 2009.

Considerations for selecting these monitoring sites included review of historical data such as toxics in fish and freshwater samples, potential for water quality improvement, and availability of a secure sampling site. Details of the selection process can be found in the QA Project Plan for this study (Johnson, 2007a; Sandvik, 2010a).

Eight of the locations selected in 2009 were a subset of the sites monitored in the previous two years. Only one waterbody (the Spokane River) was sampled in the fall but at two locations as part of a focused study for that river: Spokane River Baseline Effectiveness Monitoring for Toxics study (Sandvik, 2009a). The two locations were at Nine Mile Dam and upstream near the border of Idaho.

Descriptions of the monitoring sites are included in Appendix B.

Passive Sampling

SPMDs are polyethylene tubes filled with neutral lipid. They mimic the bioconcentration (uptake) of organic pollutants from water by aquatic organisms (e.g., fish) without the variability introduced by movements, growth, and spawning of fish (Huckins et al., 2006; USGS, 2008). Large chemical residues accumulated in SPMDs give a strong analyte signal, translating into parts-per-trillion detection limits or lower. Residues from SPMDs are used to model time-weighted average dissolved concentrations for the chemicals of interest.

In water, the amount of chemical absorbed by an SPMD is proportional to the dissolved concentration in the local water column. Total or whole water chemical concentrations determined from SPMDs are estimates based on the modeled dissolved concentration and the organic carbon-water equilibrium partitioning coefficient (K_{oc}).

To account for the effects of temperature, water velocity, and biofouling on SPMD sampling rates, an in-situ calibration method is applied using permeability/performance reference compounds (PRCs). PRCs are (analytically) non-interfering compounds with moderate to high tendency to escape and that do not occur in significant concentrations in the environment. The rate of PRC loss during a sampling period is related to the uptake of the target compound. Based on studies by Huckins et al. (2002), the difference between measured concentrations of an analyte and the PRC-derived estimates of concentrations should be within a factor of 2.

The uncertainty factors (standard deviations) for multiple sampling rates derived from the PRCs reported in this study were about ± 1.4 fold, ranging from 1.1 to 2.2 among samples.

Details of SPMD theory, construction, and applications can be found at wwwaux.cerc.cr.usgs.gov/SPMD/index.htm and in Huckins et al. (2006) and Alvarez (2010).

Timing and Placement of SPMDs

The SPMDs were deployed for approximately 28 days, from April 5 – June 1 (spring) and September 3 – 30 (fall). Deployments during these periods captured typical seasonal high-flow (spring) and low-flow (fall) conditions for the rivers. Studies have shown that peak levels of the target chemicals tend to occur during these periods (Johnson et al., 2004; 2005). For Lake Washington, these sampling events capture the higher water level (pre-stratification beginning in the spring) and the lower water level (strong stratification in the fall) (King County, 2003).

One SPMD sampler was placed at each monitoring site in a well-mixed location and away from potential point sources of the chemicals of interest. For deep-water sites, e.g., behind dams, the SPMDs were positioned in the top 20 feet of the water column, above the summer thermocline. For sites in the shallower rivers, SPMDs were placed approximately one foot above the bottom.

During the spring sampling event, replicate samplers were deployed in three of the eight waterbodies sampled (Lower Columbia, Yakima, and Spokane Rivers) to provide an estimate of variability in the field samples. Replicates were not deployed in the fall because of limited budget.

For both spring and fall, field-trip blanks were exposed to air during deployment and retrieval to assess background air contamination at each waterbody except Lake Washington.

Chemical Analyses

Chemicals analyzed at each site included over 30 CPs or breakdown products, 209 individual PCBs or congeners, 22 PAHs, and 13 PBDE congeners. A complete list of target analytes is in Appendix C.

Total suspended solids (TSS) and total organic carbon (TOC) were determined at the beginning, middle, and end of each sampling period at each site. Water temperature was monitored continuously during deployment at all sites.

Brief descriptions of contaminants included in this monitoring program are presented below.

Chlorinated Pesticides (CPs)

CPs include a number of legacy insecticides that do not degrade or metabolize easily, making them extremely persistent in the environment. They have low solubility in water but a strong affinity for lipids (fats), therefore accumulating to high concentrations in fatty tissue through the food chain (EPA, 2000).

Many CPs are neurotoxins and may cause cancer (EPA, 2000). Most were banned from use in the United States during the 1970s and 1980s as their hazards became evident (e.g., DDT). Other CPs currently used in agriculture are less persistent in the environment. However, the U.S. Environmental Protection Agency (EPA) recommends monitoring some of these (e.g., chlorpyrifos and endosulfan) because of their toxicity and potential to build up in tissue.

Polychlorinated Biphenyls (PCBs)

PCBs are chemically and physically stable synthetic organic compounds having excellent insulating properties. Hence, transformers and other electrical equipment, inks, paint, plastics, pesticide extenders, and a variety of other applications used PCBs. Manufacturing of PCBs in the United States ended in 1979 due to their toxicity and persistence in the environment.

PCBs have low solubility in water yet have a high affinity for sediments and animal fats, allowing them to readily build up in the aquatic food chain (EPA, 1999b). Health effects from PCBs include toxicity to the nervous, endocrine, digestive, and immune reproductive systems. EPA currently classifies PCBs as a probable human carcinogen based on evidence in animal studies and inadequate, but suggestive, evidence in humans (IRIS, 2009; ATSDR, 2000).

Individual PCB compounds differ from one another in the number and relative positions of chlorine atoms that they contain (1 to 10). Up to 209 different compounds are possible. Commercial PCB congener mixtures were known in the United States by the trade name Aroclor. Historically, many studies analyzed for PCB Aroclor mixtures, but increasingly more studies, including the present effort, are analyzing all the individual congeners for a more thorough assessment of toxicity potential. The term “total PCBs” refers to the sum of individual congeners or Aroclors.

Polybrominated Diphenyl Ethers (PBDEs)

PBDEs are a group of brominated organic compounds added as a flame-retardant to a variety of plastic and foam products such as electronic enclosures, wire insulation, adhesives, textile coatings, foam cushions, and carpet padding. Individual PBDE congeners differ by the number and position of bromine atoms (1 to 10) creating as many as 209 individual congener possibilities. PBDEs are often categorized by the number of bromine atoms attached to the biphenyl rings: mono- through decabromo-congeners can exist.

Penta-BDE, Octa-BDE, and Deca-BDE are the three main types of PBDEs in consumer products worldwide, with North America having the highest volume of production (Ecology and WDOH, 2006; ATSDR, 2004). Commercial PBDE products are mixtures. The mixtures are named after the primary PBDE component. In this study, PBDE results refer to the individual compound and not the commercial mixtures.

PBDEs are ubiquitous in the environment, and concentrations in humans and wildlife are increasing throughout the world. The lower bromated congeners associated with the Penta formulation in commercial mixtures (e.g., PBDE-47, 99, 100, 153) are the most bioaccumulative and make up the brunt of the levels found in animals and humans. The highest levels of PBDEs in human tissue have been found in the U.S. and Canada (Ecology and WDOH, 2006). PBDE-209 (Deca-BDE) is the most prevalent congener found in sediment and indoor dust. Deca-BDE can debrominate to lower congeners, but its contribution to the levels found in animals and humans is unclear.

Animal studies show that PBDEs can affect the thyroid, liver, immune system, nervous system, and endocrine system (Ecology and WDOH, 2006; ATSDR, 2004). EPA found available information inadequate to assess the carcinogenic potential of PBDE-47, 99 and 153 but found “suggestive” evidence regarding the potential for Deca-BDE to cause cancer in humans.

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a group of organic contaminants formed during the incomplete burning of coal, oil, gasoline, garbage, wood, or other organic substances. They are found in the environment as complex mixtures. PAHs occur naturally (i.e., forest fires and volcanoes) or can be anthropogenic. Manufactured PAH compounds are used in medicines and to make dyes, plastics, and pesticides. Other PAH compounds are found in asphalt, crude oil, coal, coal tar pitch, creosote, and roofing tar.

PAHs are generally associated with particulate matter; however, the compounds can be found in vapor form and in water (ATSDR, 1995). Principal sources of PAHs to the environment are believed to be from open burning, vehicles, heating and power plants, and industrial processes (ATSDR, 1995; Van Metre et al., 2000). Factors such as the type and quantity of fuel, the temperature and duration of combustion, and the availability of oxygen determine the nature and extent of PAH formation.

PAHs are toxic to mammals, aquatic life, plants, and several are known to cause cancer (ATSDR, 1995).

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Methods

Field Procedures

Standard SPMDs were prepared by Environmental Sampling Technologies (EST), St. Joseph, Missouri (www.est-lab.com/index.php). SPMDs are composed of a thin-walled, layflat polyethylene tube (91.4cm x 2.5cm x 70-95µm thickness) filled with 1 mL of neutral lipid triolein (purity 99.9%).

EST prepared and spiked each membrane with performance reference compounds (PRCs) consisting of 40 ng each of PCB-004, -029, and -050. EST preloaded the SPMD membranes onto carriers then shipped them frozen in solvent-rinsed metal cans filled with argon gas.

Ecology staff transported the cans with SPMDs to the field on bottled ice. Upon arriving at the sampling site, an anchoring and tethering system was constructed for securing the SPMD canisters. Standard operating procedures were used to deploy and retrieve the SPMDs (Johnson, 2007b). The cans were carefully opened; five carriers were slid into a 30 cm x 16 cm stainless-steel canister; and the canister was inserted inside an 18-inch shade device cylinder (Figure 2). Shade devices were employed to protect against photo degradation of light-sensitive compounds such as PAHs. The device was secured in the water as quickly as possible to limit air contamination. Field personnel wore nitrile gloves and avoided touching the membranes.

Figure 2. SPMDs Inside a 5-Membrane Canister and Inserted in a Shade Device Cylinder.

Ecology staff checked the SPMDs midway through the month-long deployment. At midcheck, the SPMD samplers were gently moved back and forth under water to remove loose sedimentation or biofouling. Retrieval procedure was essentially the reverse of deployment. All

SPMDs were successfully retrieved during 2009. The cans holding the SPMDs were sealed and kept at or near freezing for shipping to EST for extraction. Samples were identified and recorded, and custody was maintained at all times following Ecology's chain-of-custody procedures.

To confirm that SPMDs remained submerged throughout the sampling period, an Onset StowAway® TidbiTs™ temperature monitor was attached to each SPMD canister. Another TidbiT™ was secured out of the water near the site. These TidbiTs™ recorded water and air temperature every two minutes. Examination of the charted water and air temperature data showed that all samples remained submerged during deployment except the Yakima River replicate. That sample was not processed because it was compromised in the field.

Grab samples for TOC and TSS were collected at the beginning, middle, and end of each deployment sampling period according to Ecology SOPs (Joy, 2006; Ward, 2007) (Table 1). These samples were held on ice and shipped within the holding time (MEL, 2008) to Ecology's Manchester Environmental Laboratory (MEL) with a chain-of-custody record.

Table 1. Field Procedures for Ancillary Water Quality Parameters.

Parameter	Minimum Sample Size	Container	Preservation	Holding Time
TSS	1000 mL	1 L poly bottle	Cool to 4ºC	7 days
TOC	50 mL	123 mL poly bottle	HCL to pH<2, 4ºC	28 days

HCL = hydrochloric acid.

Water temperature and conductivity were measured in-situ during each collection using a temperature/conductivity probe (Hanna DIST 5 pH/EC/TDS meter) or an alcohol thermometer and Beckman conductivity meter. Use of these instruments followed manufacturer's instructions. Flow information and data were obtained from Ecology's Environmental Assessment Program Freshwater Monitoring Unit, USGS, and other sources.

Laboratory Procedures

Analysis

After retrieval from the field, Ecology staff sent the SPMD membranes to EST for preparation and extraction (described below) before further analyses by other laboratories. MEL analyzed CPs, PAHs, and PBDEs. Analytical Perspectives Laboratory (Wilmington, NC) analyzed PCB congeners. MEL also analyzed conventional water quality samples. Analytical methods are shown in Table 2.

For PCB congeners, extraction standards were added after the extraction process rather than before, deviating from Method 1668A. PCBs analyzed in 2007 and 2008 were processed the same as 2009 by spiking extraction standards into the extract rather than the SPMDs.

Table 2. Laboratory Procedures.

Analysis	Sample Matrix	Sample Preparation Method	Analytical Method
CPs	SPMD extract	Dialysis/GPC[1]	EPA 3620, 3665, 8081[2]
PBDEs			EPA 8270[3]
PAH			EPA 3630B/8270[3]
PCBs			EPA 1668A[4]
TOC	Whole water	NA	SM5310B
TSS			SM2540D

[1] EST SOPs E14, E15, E19, E21, E32, E33, E44, E48.
[2] Modifications of EPA SW-846.
[3] GC/MS SIM = gas chromatography / mass spectrometry applying selective ion monitoring.
[4] HRGC/HRMS = high resolution gas chromatography / high resolution mass spectrometry.
NA = not analyzed.

SPMD Preparation, Extraction, and Cleanup

Upon receiving the SPMDs, EST inspected and cleaned all membranes. For the spring samples, each sample was spiked with surrogate compounds prior to extraction. Surrogates included 50 ng each of PCB-014, PCB-078, and PCB-186 which were prepared by EST, as well as surrogates prepared by MEL which were 2000 ng of PAH and 400 ng of combined pesticide and PBDE surrogates. Fall samples received only PCB and PBDE surrogates, but at the same concentrations as the spring samples. Recovery of the surrogates provides estimates of recovery of target compounds in each sample.

EST extracted the membranes from each SPMD sample using dialysis. The extracts from each membrane were combined into a single sample and solvent exchanged to methylene chloride for gel permeation chromatography (GPC) cleanup. After GPC, the extracts were solvent exchanged into hexane, split 50:50, and each fraction sealed in a 5-mL ampoule for transport to the laboratories. One ampoule was sent to MEL. The other ampoule was sent to Analytical Perspectives (via MEL). EST's extraction and cleanup methods are documented in SOPs on file at Ecology headquarters.

The MEL ampoule was further split 50:50 for pesticide and PBDE/PAH analysis for the spring samples, resulting in 25% fraction for each. The fall samples were not split. The PBDE/PAH extract was solvent exchanged into iso-octane prior to analysis. The pesticide fraction was concentrated and then eluted through a macro Florisil® column. Following a solvent exchange concentration, the extracts were split and one portion was treated with concentrated sulfuric acid to remove PBDE interferences. Both portions were analyzed by dual column GC-ECD. No additional cleanup was performed on the samples for PAH analysis.

Analytical Perspectives analyzed the extracts for PCB congeners. A multi-column cleanup step was performed, and each extract was brought to a fixed volume. Extraction, cleanup, and injection standards were spiked into each extract at various steps for measuring the analytical performance throughout the cleanup and analytical procedures.

All results were corrected for all dilutions and reported them as ng/sample, the sample being 100% of the extract. The amount of analyte found in the extract from the sample is referred to as the “residue”.

Data Reduction

Reducing the SPMD residue (referred to as *extract*), data include: evaluating the results for usability, correcting for sample contamination where possible, and then estimating dissolved and whole-water concentrations using models provided by USGS and Meadows et al. (1998).

Correction for Background Contamination (or Blank-Correction)

Ecology evaluated sample results for usability and corrected for background blank contamination following the concepts in Method 1668A (EPA, 1999a) and Ecology’s SOP for SPMD data processing (in development). The main steps in this blank-correction process included: (1) selecting a blank to use in correction; (2) determining which results could be corrected; and (3) applying the correction where possible, qualifying results, and reviewing the impact of blank-correcting the data. This process is described below.

Field-trip blanks were used to adjust the chemical concentrations reported in the SPMDs because the field-trip blank represented contamination from both the field and laboratory environment. In most cases, the chemical residues in field-trip blanks were similar to the Day0-dialysis laboratory blanks[2]. More than 80% of detected results from the field-trip and Day0-dialysis blanks agreed within ≤25% relative standard deviation (RSD) or relative percent deviation (RPD) for the spring and fall. Some field-trip blanks tended to have lower values than the Day0-dialysis blanks, which may indicate some loss of contaminant in the field while the SPMDs are exposed to air during deployment and retrieval.

Higher RSD and RPDs between the field-trip blank and the Day0-dialysis blank were more common where detections were near or below the reporting limit. Multiple field-trip blanks in the spring were more representative among sites and better describe the variability seen between the field-trip and Day0-dialysis blanks.

The sample results were evaluated to determine if they could be blank-corrected. Results that were greater than the mean plus two standard deviations of the field-trip blank were deemed correctable. Correctable results were adjusted by subtracting the mean of the field-trip blanks from the result; the adjusted results were then qualified as estimates with unknown bias (JK).

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[2] The Day0-dialysis blank is a laboratory blank used to represent background contamination during post-deployment processing including dialysis and cleanup. This blank also serves as reference for PRC loss. This blank uses five SPMD membranes from the same batch of membranes that are used for all other samples.

For detected compounds that did not meet the blank-correction criteria, the original result was used as an estimated reporting limit and qualified as being below the method detection limit with an unknown bias (UJK). The detection limit was used where a compound was not detected.

The fall sampling event provided only one field-trip blank. This result was assumed to represent the mean background contamination for that period because the samples were in the same waterbody (the Spokane River) and were reasonably close in proximity (approximately 26 miles apart). The standard deviation of the fall field-trip blank was estimated using the proportion of the standard deviation to the mean of the spring field-trip blanks. The assumption was made that the proportion of standard deviation to mean for one sampling period is similar to another sampling period. Even though this approach limits representativeness, the assumption seems fair, as based on the review of the spring and fall field-trip blank results (see *Data Quality* section).

Once evaluated, the spring and fall sample results were blank-corrected and qualified as described above.

The impact of the correction process varied among the chemical groups. Pesticide results were deemed usable without any correction process since no contamination was found in the field-trip blanks. PAHs had 66% detected results with 66% of those correctable. For the combined spring and fall PBDE results, 53% were detected, and of those detected, only 40% were correctable. For spring and fall PCBs, 89% were detected with 75% of those correctable.

Some results fell below the original reporting limit after they were blank-corrected. These results were considered detected at the "new" corrected level in the remainder of this report.

Methods for Estimating Chemical Concentrations in Water

Dissolved Water Concentrations

SPMDs only absorb the dissolved form of a chemical. The concentrations of absorbed residues are determined from laboratory analyses and blank-correction procedures as described above. These concentrations can be converted to a time-weighted average dissolved water concentration that can be compared with data from other sampling methods.

Dissolved concentrations for the chemicals of interest were estimated using the most current version of the USGS Estimated Water Concentration Calculator model. This model was downloaded from the USGS website for Columbia Environmental Research Center (CERC) Integrative Passive Samplers (USGS, 2008): www.cerc.usgs.gov/Branches.aspx?BranchId=8.

Ecology entered the data collected on chemical residues, exposure times, and PRC recoveries in the present 2009 study into the USGS model for the available analytes. Residue data are available from the authors of this report. Exposure times and PRC data are listed in Appendices D and E.

The USGS model uses the octanol-water partition coefficient constant (log K_{ow}) for each analyte to estimate dissolved water concentrations. The model provides log K_{ow} values for many bioaccumulative chemicals. For those analytes missing log K_{ow}s in the model, literature values were used. If multiple log K_{ow} values were found, a mean was selected using the t-test at 95% confidence for rejection of outliers (USGS, 2008; Alvarez, 2008).

Where log K_{ow}s could not be found in the literature, K_{ow}s were calculated using an atom/ fragment calculation developed by Syracuse Research Corporation (Meylan et al., 1995). Log K_{ow}s for analytes PBDE-49, -71, -184, -191 were estimated using similar chemicals (PBDE-47, -69, -183, -190, respectively). This approach seemed reasonable based on other PBDE congeners that are consecutive to each other and have similar log K_{ow}s. USGS estimated the log K_{ow} for chlorpyrifos from endrin because of endrin's proximity in log K_{ow} values (USGS, 2008).

In view of the uncertainties previously stated, all chemical concentrations in water calculated in this report should be considered estimates. Log K_{ow}s used in estimating these concentrations can be found in Appendix F.

Analytes Expressed as Sums

Several analytes are reported here as summed values of detected compounds that belong to a group having similar characteristics. For example, total DDT is the sum of o,p'- and p,p'-isomers of DDD, DDE, and DDT. Total chlordane is the sum of *cis* and *trans* chlordane, *cis* and *trans* nonachlor, and oxychlordane. Endosulfan, unless specified, is the sum of alpha (endosulfan I) and beta endosulfan (endosulfan II). Total PCB is the sum of the individual congeners. Total PBDE is the sum of the 13 congeners analyzed in this study.

Low molecular weight PAH (LPAH) represents the sum of the following low molecular weight PAH (< 4 aromatic benzene rings):
- Naphthalene.
- Acenaphthylene.
- Acenaphthene.
- Fluorene.
- Phenanthrene.
- Anthracene.

High molecular weight PAH (HPAH) represents the sum of the following high molecular weight PAH (5-6 aromatic benzene rings):
- Fluoranthene.
- Pyrene.
- Benz(a)anthracene.
- Chrysene.
- Total benzofluoranthene ("B," "J," and "K" isomers).
- Benzo(a)pyrene.
- Indeno(1,2,3,-c,d)pyrene.
- Dibenzo(a,h)anthracene.
- Benzo(g,h,i)perylene.

Total PAH is the sum of LPAH and HPAH.

Non-detect results were treated as zero when summing compounds for total DDT, total chlordane, total PAH, total PBDE, and total PCB. All summed compounds were calculated from water concentration values (as opposed to the residue concentration).

All data qualifiers were retained for residue results in the data appendices.

Total Water Concentrations

Organic compounds in water partition between dissolved and particulate fractions. The "total" concentration is the sum of dissolved and particulate fractions.

In this 2009 study, total water column concentrations were estimated from the dissolved data using an equation from Meadows et al. (1998):

$C_{w\text{-}tot} = C_w (1 + TOC (K_{oc}/M_w))$

where:
- $C_{w\text{-}tot}$ is the total water concentration.
- C_w is the dissolved concentration.
- TOC is total organic carbon (average of three samples per deployment period).
- K_{oc} is the organic carbon-water equilibrium partition coefficient.
- Mw is the mass of water (1g/mL).

TOC is critical in determining chemical uptake rates of compounds with high log K_{ow}s because of TOC's effect on the dissolved fraction. The higher the K_{ow}, the greater the affinity of the compound has for suspended organic matter. There is therefore a lower tendency for these compounds to be transported in the dissolved phase. Limited water solubility coupled with increased binding to TOC, limits the amount of the compound in contact with the SPMD membrane (Meadows et al., 1998). K_{oc} values were derived using Karickhoff's (1981) approximation $K_{oc} = 0.411K_{ow}$.

Comparison of Methods Used for Blank Correction and Estimating Chemical Concentrations in Water

The comparability of different data-reduction practices used in this study to date was determined by examining the field deployment, sample, and data-reduction processes. Only results sharing the same sampling locations and analysis were compared.

The data were considered comparable among the years (2007, 2008, 2009) because the sampling procedures (i.e., field deployment, sample processing) were the same and the result processing was nearly the same. There were two main differences in how results were processed: (1) blank correcting all results versus blank correcting only results that were deemed acceptable for blank correction, and (2) using summed PCB values (e.g., total PCBs) verses individual congeners as inputs into the USGS model used for estimating PCB concentrations in water.

Comparison of Blank Correction Procedures

The 2008 and 2009 sample results were evaluated and blank-corrected as described in the *Data Reduction* section above. The 2007 sample results were simply blank-corrected without any evaluation because there was only one field-trip blank for each sampling event (spring and fall) in 2007. All blank-corrected results were qualified as estimates for all three years.

To determine the effects of different blank correction methods, the 2008 and 2009 PCB and PBDE results were blank-corrected using both methods above: then the RPDs between the results were examined.

Overall, both blank correction methods affected results by lowering the congener's contribution to the sum total of the analyte. For PCBs, the RPDs between results from the two blank correction methods were generally less than 10%. The higher RPDs (up to 27%) were for the lowest result values where small differences yield large RPDs.

For PBDE results, the RPDs from the different blank-corrected methods were much higher (many >50%) because most of the results reported were near or below the reporting limits. Those samples that had elevated PBDEs (e.g., >50ng/sample such as found in the Spokane River) had RPDs of less than 10%. Therefore, PBDE results were considered comparable for samples with congener results above the reporting limits. Results near or below the reporting limit were within background noise, which clouded comparability. These PBDE results should be considered categorically as "low" rather than a definite concentration level even though there is a value listed at these low levels.

Other analytes were processed the same in all three years. CPs did not need blank correction in any years because no analytes were found in the blanks except for Lindane in three spring samples in 2007. Two of those results were qualified as not detected. The third sample was blank correctable.

PAH results were processed the same in 2008 and 2009. They were not analyzed in 2007.

Water Concentration Comparisons

The same USGS model was used for all years for estimating water concentrations. However, the 2007 PCB congener results were totaled and then blank-corrected before estimating water concentrations, whereas the 2008 and 2009 PCB congener results were blank-corrected and run through the water concentration model on an individual congener basis before totaling PCBs. When comparing both methods of estimating water concentrations using the previous and current results (2008 and 2009), RPDs were less than 10% overall, which is adequate for considering the results comparable.

PBDEs were blank-corrected and run through the model as individual congeners for all years.

Data Quality

The QA Project Plan (Johnson, 2007a) defined measurement quality objectives (MQOs) for accuracy, bias, and reporting limits for this project. Various QC samples were analyzed to help determine if MQOs were met. These samples included surrogates, blanks, replicates, matrix spikes, and control samples from the laboratory, as well as replicates and various types of blanks from the field. The quality of data is summarized below. Part 2 of this report has more detail on routine quality control (QC) efforts as well as the extended efforts done in the spring of 2009.

Laboratory

Based on assessments of QC results, reviews of the laboratory data packages and MEL's data verification reports (case narratives), data from the laboratories were accepted, accepted with appropriate qualifications, or rejected. See Part 2 of the report for more detail.

Field

Sample Integrity

The SPMDs were checked midway through the 28-day deployment period. During this check, SPMD samplers were gently moved back and forth under water to remove loose sediment or biofouling. All but one of the samplers remained submerged based on data from continuous temperature monitoring devices (TidbiT™) which were attached to the sampler and attached on shore nearby. All SPMDs were retrieved for the 2009 spring and fall sampling events.

Matrix Spike, PRC, and Surrogate Recoveries

Various spiking practices were used in the preparation and processing of SPMDs to help define the quality of results. For matrix spikes, all recoveries fell within the acceptable 50% - 150% recovery limits with several exceptions. Yet no sample results were qualified based on the matrix spike recoveries. The PRC and surrogate recoveries were within acceptable ranges (PRCs: 20 – 80%; surrogates: 25 – 150%) with a few exceptions. Some surrogate concentrations seemed high, and it was discovered that the surrogate concentrations were twice as high as initially reported (as determined by analysis of the surrogate solution). Appropriate corrections to the results were made.

Replicates

Replicate SPMDs were deployed in the spring at three locations: the Lower Columbia, Spokane, and Yakima Rivers. These were independent samples deployed within a few feet of each field sample. Although one replicate was compromised in the field, the other two showed good precision. In most cases, over 80% of the chemicals detected had RPDs of 20% or less. Results are listed in Appendix G. Where replicates were deployed, the values were averaged and are used in the remainder of this report.

Blanks

The spring 2009 monitoring effort included extra QC samples to help address concerns about contamination within the SPMD sampling system. This additional QC work focused on blanks in order to better understand the sources, magnitude, and variability of contamination of the sampling system. A variety of blanks were used outside the analytical laboratory. These blanks often contained low levels of target chemicals. Results from the various field blanks were then used to identify the major sources and magnitudes of contamination in SPMDs. Results showed that:

- Fabrication, storage, dialysis, and GPC processes for SPMDs account for 60% - 90% of contamination.
- The spiking processes account for 10% - 30% of contamination.
- Exposure to air during deployment and retrieval of SPMDs accounts for about 0% - 15% of contamination.
- Contamination from the analytical laboratories currently used seems inconsequential.

The level of “background” contamination varied among analytes during the 2009 spring effort and varied between two sampling events for each group of analytes:

- Total PBDEs: 30-55 ng/sample in 2009 spring; and 50-75 ng/sample in 2008 fall.
- Total PCBs: 25-35 ng/sample in 2009 spring; and 35-40 ng/sample in 2008 fall.
- Total PAHs: 300-500 ng/sample in 2009 spring; and 430-570 ng/sample in 2008 fall.

The levels of contamination found in different blanks, relative to levels found in the samples, confound data interpretation and will likely limit the ability of this project to detect temporal or spatial trends in contaminant levels

Data Quality Assessment

Data quality assessment is the evaluation of data to determine if the data can support their intended use (EPA, 1998). Results from field and QC samples were reviewed to determine whether data collected using the SPMD system for this study are suitable for the purpose of trend detection.

Ability to Detect Trends

Signal verses Noise

Ideally, levels of contaminants in the environment (the signal) would be well above the noise of the sampling and analytical system. Yet if contaminant levels in the environment are close to the level of noise in the measurement system, the signal from the environment gets lost in the noise, which confounds attempts to determine true change in the environment. Unfortunately, this situation exists for the majority of sites and target analytes that have been monitored thus far in this trend monitoring effort.

The ability to detect contaminant trends depends on at least two conditions:

- Sample results are not unduly influenced by noise in the measurement system. In this project, the greatest noise is manifested in contamination of blank samples.
- The levels of target analytes at sites are high enough so that a trend could be detected before the levels decline to a point where they cannot be discerned from the noise in the measurement system.

There are common practices for addressing contamination of the measurement system. Blanks are widely used to help characterize the sources and levels of noise in a measurement system. Generally, EPA guidance deems any result that is less than five times (5x) the level found in the blank should be rejected (EPA, 1999c). This "5x" rule is widely used, including for other Ecology projects. The 5x rule gives a greater confidence that the result obtained is not unduly influenced by contamination in the sampling system. For high resolution mass spectrometry (HRMS) analyses, such as for dioxin/furans and PCB congeners, MEL applies a 10x rule even though EPA guidance (EPA, 2002) is less specific in these cases. For HRMS methods, sample results that are less than 10 times the value of contaminant found in the blank are flagged by MEL as "non-detect" values.

While use of blank-correction techniques can reduce some of the noise, blank-correction is controversial, partly because it is prohibited when using most analytical procedures. The EPA Method 1600 series does allow blank-correction yet specifies a rigorous procedure for blank-correction. This rigorous procedure has not been followed in Ecology SPMD studies because of the cost of doing so. Instead, Ecology SPMD studies have used a variety of less rigorous blank-correction techniques, sometimes leading to controversy over interpretation of study results.

Contaminant Thresholds for SPMDs

The ability to detect contaminant trends in this project must estimate the thresholds (ambient levels of target analyte) at which trends could be measured using SPMDs. The following estimation does not include the blank-correction process described in the *Data Reduction* section above, which might improve the sensitivity of trend detection if the technique were not controversial.

The following two points describe the thresholds representing the low and high values that should frame the ending and beginning points of a trend monitoring effort:

1. The concentration *after* some decrease over time should be well above the noise of the measurement system. This would be a minimum of 5 times the level found in the blanks. A more conservative level would be 10 times the level found in the blanks, a level which is often characterized as the reporting limit when blank contamination is evident. The variability of the level of blank contamination over time is poorly understood. This suggests that using a level that is 10 times the value of the blanks would improve the chances of measuring true values versus noise in the system.

2. The initial concentrations measured *before* decrease over time should be high enough that a decrease is detectable and can be attributed to actual change over time. Such a decrease would need to be a strong signal for this project because of the low frequency of sampling (1-2 samples per year), high variability of the data, and challenges in quantifying levels of organic analytes. A likely manifestation of a strong signal would be a large reduction, such as a change by a half to a full order of magnitude. In this case, the pre-trend value would then need to be 5 to 10 times greater than the post-trend value. Using a level that is 10 times the value of the blank as a post-trend value (from #1 above), the pre-trend value would then need to be 50 to 100 times greater than the value found in the blanks (i.e., value found in blank times 10, then times 5 to 10, which equals 50 to 100 times the value found in the blanks).

The ability to detect a trend with a weaker signal, such as a reduction by a factor of 2-5, seems less likely given the variability associated with using SPMDs. A weaker signal will be obscured by uncertainty or variability from a combination of factors: the sample collection system (SPMDs), analytical methodologies for organic chemical, and variability associated with the inputs for the model that's used for estimating water concentrations.

Recommended Contaminant Thresholds for SPMD Trend Monitoring

For this project then, continued monitoring for trends might be worthwhile where the ambient levels of target analytes are at least 50 times greater than what is measured in the blanks. Table 3 shows threshold values for selected analytes (SPMD residue values). Note that the chlorinated pesticides in Table 3 have not been detected in blanks, so the threshold for continued monitoring is set at only 5 to 10 times the reporting limit.

Table 3. Values for Selecting Thresholds for Continued Trend Monitoring (ng/sample).

Characteristic	PBDEs	PCBs	DDTs	Dieldrin	Chlor-pyriphos	Endo-sulfan	Penta-chloro-anisole	Toxa-phene
Mean of Trip Blanks	46	65	10 U	10 U	10 U	10 U	10 U	100 U
10x Mean of Trip Blanks = Reporting Limit	460	650	10	10	10	10	10	100
Threshold for Continued Monitoring (50-100x mean of trip blank, or 5-10 times the reporting limit)	2300-4600	3250-6500	50-100	50-100	50-100	50-100	50-100	500-1000

U - analyte not detected at the associated reporting limit.
Mean of trip blanks based on 2007-2009 PBT Trends project only.

Recommended Monitoring Sites for the PBT Trend Study

Table 4 summarizes the possibility of detecting trends at monitored sites. Selected pesticides in the Yakima and Walla Walla Rivers are the most promising for trend detection because ambient levels are high relative to reporting limits. While levels of PCBs and PBDEs in the Spokane River do not meet the 50x threshold, the interest in this site may warrant continued monitoring, with the understanding that detection of a true trend will be challenging. PCBs in the Yakima River show a low possibility for trend detection, yet a recommendation to continue monitoring seems reasonable because PCB levels continue to exceed human health criteria in water and fish. While the Lower Columbia River site shows low possibility for detecting trends in most analytes, this site is valuable because it represents a large river basin and also is used by other monitoring programs (e.g., USGS, Oregon Department of Environmental Quality). The Queets River site remains valuable as a reference site, with all analytes found at low levels.

Table 4. Qualitative Summary of the Possibility of Detecting Trends at Monitored Sites.

Site	PBDEs	PCBs	DDTs	Dieldrin	Chlor-pyriphos	Endo-sulfan	Penta-chloro-anisole	Toxa-phene
Yakima River	u	L	H	L	M	M	M	M
Walla Walla River	u	u	H	L	H	M	M	H
Spokane River at Nine Mile Dam	M	L	u	u	u	u	u	u
Lower Columbia River	L	L	L	u	u	M	M	L
Queets River	R	R	R	R	R	R	R	R
Middle Columbia River	u	L	M	u	u	L	M	u
Upper Columbia River	u	u	H	u	u	L	M	u
Lake Washington	u	u	u	L	u	u	M	u

H, M, L - high, medium, and low possibility for detecting decreasing trend.
R- reference site.
u - unlikely to detect decreasing trend.

Ambient levels of target analytes at most sites are so low that trend monitoring would be a risky endeavor, yet this and other factors should be considered when deciding whether to continue monitoring:

- Likelihood of detecting true change over time.
- Importance of the target analyte and detecting change in it over time.
- Stability of the measurement system (e.g., data gaps, changes in methodology).
- Cost of monitoring over time.

Considering all factors, recommendations are:

- For 2011, monitor the five sites in Table 5 for the designated analytes.
- For 2012, suspend monitoring at all sites in order to:
  - Analyze results from all years and test for trends.
  - Evaluate the effects of corrective actions.
  - Review recent changes in SPMD methodology from USGS.
  - Review the entire monitoring effort.
  - Recommend future actions.

Table 5. Sites and Analytes Recommended for Continued Monitoring.

Site	PBDEs	PCBs	CPs
Yakima River	--	X	X
Walla Walla River	--	--	X
Spokane River at Nine Mile Dam	X	X	--
Lower Columbia River	X	X	X
Queets River	X	X	X

Results and Discussion

Streamflow Conditions

Streamflows were higher in spring 2009 than average historical spring flows. These higher levels were due to above normal temperatures melting accumulated snow in the mountains during May and the first part of June.

Fall flows in September 2009 were somewhat lower than normal on the western side of Washington and lower yet on the eastern side of the state. Actual precipitation in the form of rain or snow was lower than normal, setting up drought conditions particularly on the eastern side of the state. Flow data are provided in Appendix H.

Ancillary Water Quality Data

The results for TSS, TOC, and conductivity at the SPMD monitoring sites are listed in Appendix I. Results were similar to previous years (2007 and 2008), which suggests the same pattern of higher values in the spring than in the fall. Since only the Spokane River was sampled in the fall, comparisons of TSS and TOC are restricted to that waterbody for 2009.

Average TSS in the spring ranged from 2.7 – 96 mg/L for all sites and was 7.0 mg/L for the Spokane River. TSS for the two Spokane River sites in the fall averaged 1.0 (not detected) to 2.0 mg/L, upstream and downstream respectively. TOC for all sites in the spring averaged 1.0 – 7.6 mg/L and for Spokane River was 1.7 mg/L. Fall TOC for the Spokane River averaged 1.5 mg/L upstream and 1.2 mg/L downstream.

Dissolved Chemicals

Concentrations of CPs, PCBs, and PBDEs

Summary statistics for dissolved CPs, PCBs, and PBDEs in the spring and fall of 2009 are found in Table 6. Reporting limits were used for estimating mean and median values to capture many analytes that were detected but reported as nondetects because they were not blank correctable. A total of 12 field samples were analyzed (10 in the spring and 2 in the fall). The type of chemical analyses performed varied among samples. Reporting limits were used for nondetects in calculating the statistics. The concentrations are in picograms per liter (parts per quadrillion) and are considered estimates. The data are in Appendices J and K (dissolved data). These data and SPMD residue data are also available upon request through Ecology.

Many of the 2009 results were similar to 2007 and 2008 results (Sandvik, 2009b; 2010b). Chemicals not detected in 2009 were heptachlor, alpha-benzenehexachloride (a-BHC), beta-benzenehexachloride (b-BHC), delta- benzenehexachloride (d-BHC), aldrin, endrin, endrin ketone, endrin aldehyde, mirex, and methoxychlor. These same chemicals were also not detected in 2007 or 2008.

Table 6. Summary Statistics (pg/L, dissolved) for 2009 CP (spring) (n = 7), Total PCBs (n = 12), and Total PBDEs (n = 9).

Parameter	Number of Detections	Detection Frequency	Min.	Max.	Median	Mean	Standard Deviation	90th %
Total PCBs	12	100%	5.4	130	60	66	36	125
Total PBDEs	8	89%	4.2	240	34	60	78	130
Total DDT[1]	6	86%	22	260	143	143	100	250
Chlorpyrifos	6	86%	<25	6600	200	1200	2400	3200
Endosulfan I	5	71%	<220	2200	330	590	720	1200
Dacthal (DCPA)	5	71%	20	74	26	32	19	48
Hexachlorobenzene	5	71%	<3.9	46	13	17	14	32
Pentachloroanisole	4	57%	<4.1	20	12	12	5.4	18
DDMU[2]	4	57%	<4.1	<34	12	15	10	<29
Dieldrin	3	43%	<9.7	37	12	18	10	30
Toxaphene	2	29%	<79	1000	110	250	330	510
Endosulfan II	2	29%	<460	1500	460	700	50	1200
Endosulfan Sulfate	1	14%	<320	440	320	350	50	420
Total Chlordane[3]	1	14%	<4.3	34	7.5	12	10	23
Gamma-BHC (Lindane)	1	14%	<68	<85	68	73	7.4	83
Heptachlor Epoxide	0	0%	<11	<20	13	14	2.9	<17

1. Total DDT is the sum of 2,4'- and 4,4' isomers of DDD, DDE, and DDT.
2. DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.
3. Total chlordane is the sum of cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane.

< = reporting limit for nondetects.

PCBs were detected in all samples. Total PCBs ranged from 5.4 to 130 pg/L with an average of 66 pg/L. These results were similar to previous two sampling events where PCBs were found in all samples ranging from 6.2 to 99 pg/L (in 2007) and 6.7 to 110 pg/L (in 2008) and averaged 50 and 39 respectively.

PBDEs were detected in 89% of the samples with PBDE-47 being the most frequently detected congener (89%). This pattern is consistent with previous two years and other studies showing the distribution of commercial PBDEs and its breakdown products (Sandvik, 2009b; 2010b; Ecology and WDOH, 2006; Johnson et al., 2006; and Hale et al., 2003). PBDEs were detected in 96% of the 2007 samples and 60% of the 2008 samples.

Most PBDE congeners were detected at or below the reporting limit, except for PBDE-47 and PBDE-99. PBDE-183, -184, -191, and -209 were not detected, which is similar to the last two years. Detected PBDEs ranged from 1.4 - 140 pg/L in 2009. In 2007 and 2008, detected PBDEs ranged from 0.1 - 101 pg/L and 0.48 - 130 pg/L respectively.

In general, the detections were higher for most CPs in 2009 than in 2007 or 2008. This can be explained, in part, by the fact that CPs were analyzed only in the spring of 2009. Previous results show CPs to be found more often and at higher concentrations in the spring, which could reflect soil disturbance (tillage), spring runoff, and irrigation for historical-use pesticides and the application period of the current-use pesticides (Sandvik, 2009b; 2010b).

DDT or its breakdown products (DDE and DDD) were detected in 86% of the samples. DDE and DDD were detected at this same frequency whereas the parent compound DDT was detected in 57% of the samples. A similar pattern was observed in 2007 and 2008 with DDE and DDD detected in 61 - 68% of the samples and DDT in 52% for both years. Also, DDMU, a breakdown of DDE, was found more frequently (57%) in 2009 than in 2007 (30%) and 2008 (12%) although concentrations appear low (less than 33 pg/L) overall.

Chlorpyrifos was found more frequently in 2009 (86%) than in either of the last two years (<50%). This may reflect the spring application period of this chemical as mentioned above. Concentrations were higher in 2009 (6600 pg/L) than in 2007 (3800 pg/L) or 2008 (2500 pg/L).

Endosulfan, also a current-use pesticide, was found in over half the samples for all three years. Concentrations for endosulfan varied among the years, but the highest levels (<13000 pg/L found since 2007) were more than three times lower than the water quality criteria (56000 pg/L).

Dieldrin was detected in samples at 43% compared to 40% in 2008 and 57% in 2007. Although the 2009 maximum concentrations were lower at 37 pg/L than 63 pg/L (2008) and 71 pg/L (2007), the average concentration ranged from 16 to 20 pg/L. Highest concentrations were found in the fall samples in 2007 and 2008. Since no fall samples were analyzed for CPs in 2009, dieldrin concentrations may appear lower when compared to the previous two years.

Pentachloroanisole, a microbial breakdown product of the wood preservative pentachlorophenol, was found less frequently than before: 57% in 2009, 64% in 2008, and 74% in 2007. Concentrations were very similar among all three years with maximum concentrations ranging from 20 to 37 pg/L and averaging 12 to 13 pg/L.

Concentrations of PAHs

Table 7 shows summary statistics for dissolved PAHs. PAHs were detected in all 2009 samples, which were analyzed in the spring only. Total PAHs ranged from 130 to 5300 pg/L, which was somewhat similar to 2008 values (11 to 6500 pg/L). The low value from 2008 was a fall sample, which, again, is missing for the 2009 samples. No PAHs were analyzed in 2007.

LPAH and HPAH were detected in 100% of the samples and ranged from 110 to 3600 pg/L and 25 to 1700 pg/L respectively. In 2008, the upper range was 5100 and 2700 pg/L for LPAH and HPAH respectively. Average concentrations were similar for total PAH when comparing 2008 (1800 pg/L) to 2009 (2000 pg/L).

Table 7. Summary Statistics for 2009 PAHs (n = 10) (dissolved, pg/L).

Parameter	Number of Detections	Detection Frequency	Min.	Max.	Median	Mean	Standard Deviation	90th %
Phenanthrene	10	100%	110	690	410	400	170	500
Fluorene	8	80%	<35	180	93	100	38	140
Naphthalene	4	40%	<1500	<3100	2400	2400	580	3000
Acenaphthene	4	40%	<28	200	98	100	57	200
Acenaphthylene	1	10%	<26	<140	77	94	38	<140
Anthracene	0	0%	<43	<76	50	53	9.2	<61
Total LPAH[1]	10	100%	110	3600	680	1400	1300	2880
Fluoranthene	10	100%	25	720	315	340	230	590
Pyrene	8	80%	<14	500	120	180	150	320
Benzo(b)fluoranthene	8	80%	8	150	17	32	43	64
Benzo(a)anthracene	5	50%	26	<89	37	46	20	68
Benzo(k)fluoranthene	5	50%	6.9	<61	20	26	19	45
Chrysene	1	10%	<1.7	220	26	43	64	70
Benzo(a)pyrene	1	10%	<15	<66	29	31	14	<37
Indeno(1,2,3-cd)pyrene	0	0%	<20	<81	36	40	16	<48
Dibenzo(a,h)anthracene	0	0%	<18	<71	32	35	14	<42
Benzo(ghi)perylene	0	0%	<22	<88	40	43	18	<53
Total HPAH[2]	10	100%	25	1700	380	600	500	1016
Total PAH[3]	10	100%	130	5300	990	2000	1700	3950
Retene	10	100%	56	610	200	280	210	570
Dibenzofuran	8	80%	90	160	100	110	24	140
1-Methylnaphthalene	7	70%	380	1600	880	850	370	1200
2-Methylnaphthalene	6	60%	770	2900	1800	1700	620	2100
Carbazole	0	0%	<1000	<1300	1000	1000	95	<1000
2-Chloronaphthalene	0	0%	<210	<260	210	220	16	<230

1. Total LPAH is the sum of low molecular weight PAHs: naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, and fluorene.
2. Total HPAH is the sum of high molecular weight PAHs: fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.
3. Total PAH is the sum of LPAH and HPAH.

< = reporting limit for nondetects.

Several analytes contributed the most to LPAH in all years. Phenanthrene was a consistent contributor to LPAH with a detection frequency of 100% and averaging 400 pg/L. This matched 2008 closely when 84% of the samples had detectable amounts of phenanthrene with an average of 510 pg/L. Unlike in 2008 where acenaphthene ranked second in contributing to LPAH, in 2009 fluorene was the second highest contributor to LPAH found in 80% of the samples, but only averaging 100 pg/L. This proportion could vary depending on the individual sample and the individual chemicals contributing to LPAH. For instance, several samples were more influenced by naphthalene as the second highest contributor since the concentration value was over tenfold the value of fluorene. As was the case in 2008, the background levels of naphthalene in blank samples masked naphthalene's contribution in samples having lower levels.

The major contributors to HPAH were fluoranthene and pyrene, each having detection frequencies of 100% and 80% and averaging 340 and 180 pg/L respectively. Although benzo(b)fluoranthene also had detections in 80% of the samples, the levels were generally lower ranging from 8 - 150 pg/L and averaging 32 pg/L. These two PAHs contributed over 86% of the HPAH average of 600 pg/L and consistently accounted for over 70% of HPAH for all samples individually. The same was found for the 2008 samples.

Retene was found in all the samples as it was in the 2008 samples. The concentrations were lower in the 2009 samples and ranged from 56 - 610 pg/L versus 12 - 5500 pg/L in 2008. Retene can be found in the breakdown of wood products in sediment.

Carbazole was not detected in any 2009 samples and in only a few 2008 samples (20%). Dibenzofuran was found in 80% of the 2009 samples and similarly in 84% of the 2008 samples. Both can be found in environments contaminated by coal tar and creosote among other similar products.

Spatial and Seasonal Patterns

A total of 70 chemicals were analyzed in SPMDs, but not every site was analyzed for all chemicals. Table 8 list the chemicals analyzed at each location.

Table 8. Waterbodies and Chemicals Analyzed in 2009.

Waterbody	Spring or Fall (S or F)	Chlorinated Pesticides	PAHs	PBDEs	PCBs
Lower Columbia River	S	X	X	X	X
Middle Columbia River	S	X	X		X
Upper Columbia River	S	X	X		X
Queets River	S	X	X	X	X
Yakima River	S	X	X	X	X
Walla Walla River	S	X	X		X
Lake Washington	S		X	X	X
Spokane River at Nine Mile Dam	S & F		X	X	X
Spokane River near Idaho Border	F			X	X

Results from most sites are compared below to the 2007 and 2008 spring results. Only the Spokane River at Nine Mile Dam is comparable to previous years' results from spring and fall for PBDEs and PCBs. No pesticide data were available for the Spokane River at Nine Mile Dam in the spring of 2007, because the sample was compromised in the field.

The highest concentrations of CPs and PCBs were generally found in the spring at most sites. PBDE seasonal patterns have been inconclusive and differed from one location to another.

Estimated Dissolved Concentrations

Figures 3 - 11 compare 2007, 2008, and 2009 spring and fall estimated dissolved concentrations of T-DDT, total PCBs, total PBDEs, dieldrin, endosulfan, toxaphene, chlorpyrifos, and pentachloroanisole. Concentrations for spring and fall were averaged when both field sample and replicate sample results were available (such as for 2007 and 2008 data). When calculating averages, detection limits were used for chemicals that were not detected. In some cases, blank-corrected results may show below the typical reporting limit for that chemical (e.g., dieldrin and endosulfan). Sites are ordered from the highest to lowest concentration observed in the spring of 2009.

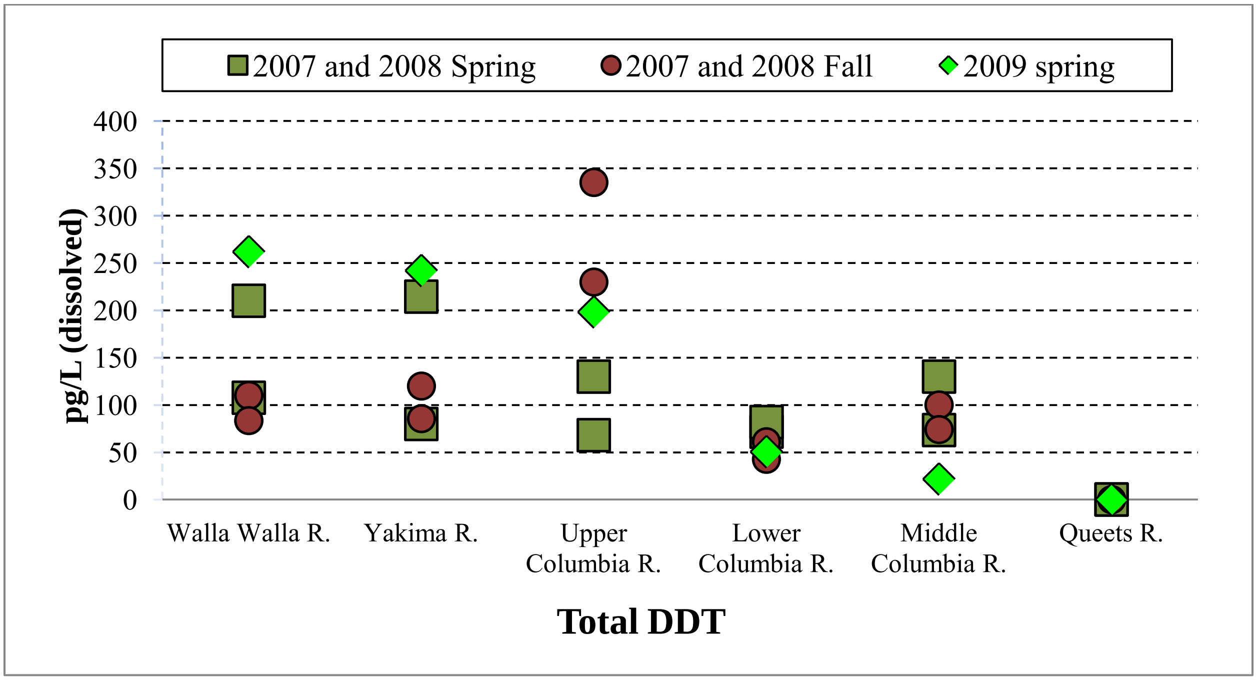

Figure 3. Estimated Dissolved Concentrations of Total DDT in 2007, 2008, and 2009 Spring and Fall.

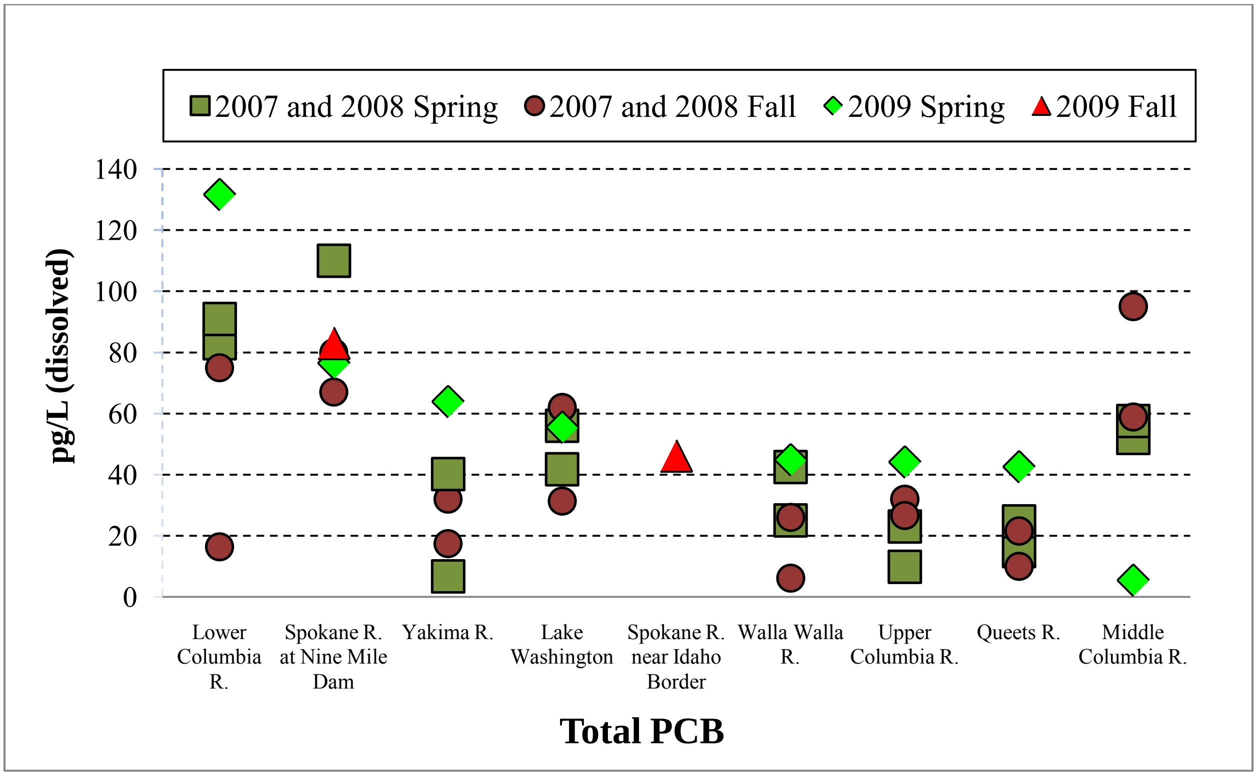

Figure 4. Estimated Dissolved Concentrations of Total PCB in 2007, 2008, and 2009 Spring and Fall.

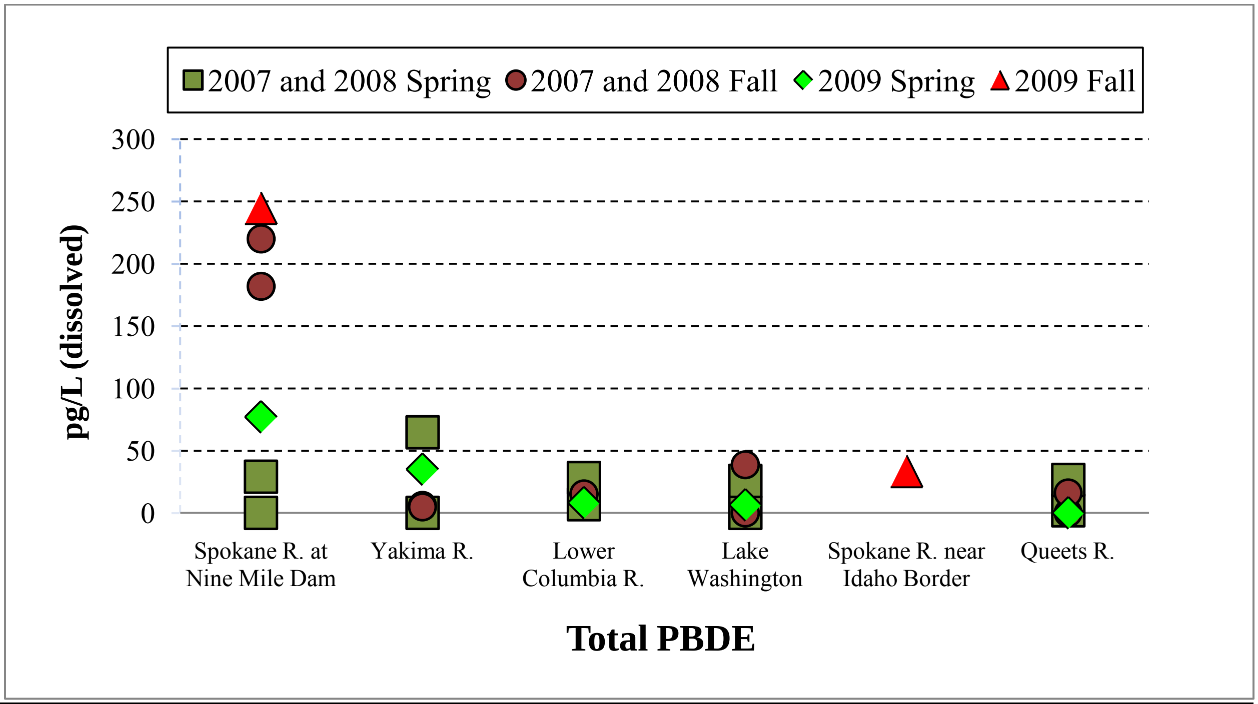

Figure 5. Estimated Dissolved Concentrations of Total PBDE in 2007, 2008, and 2009 Spring and Fall.

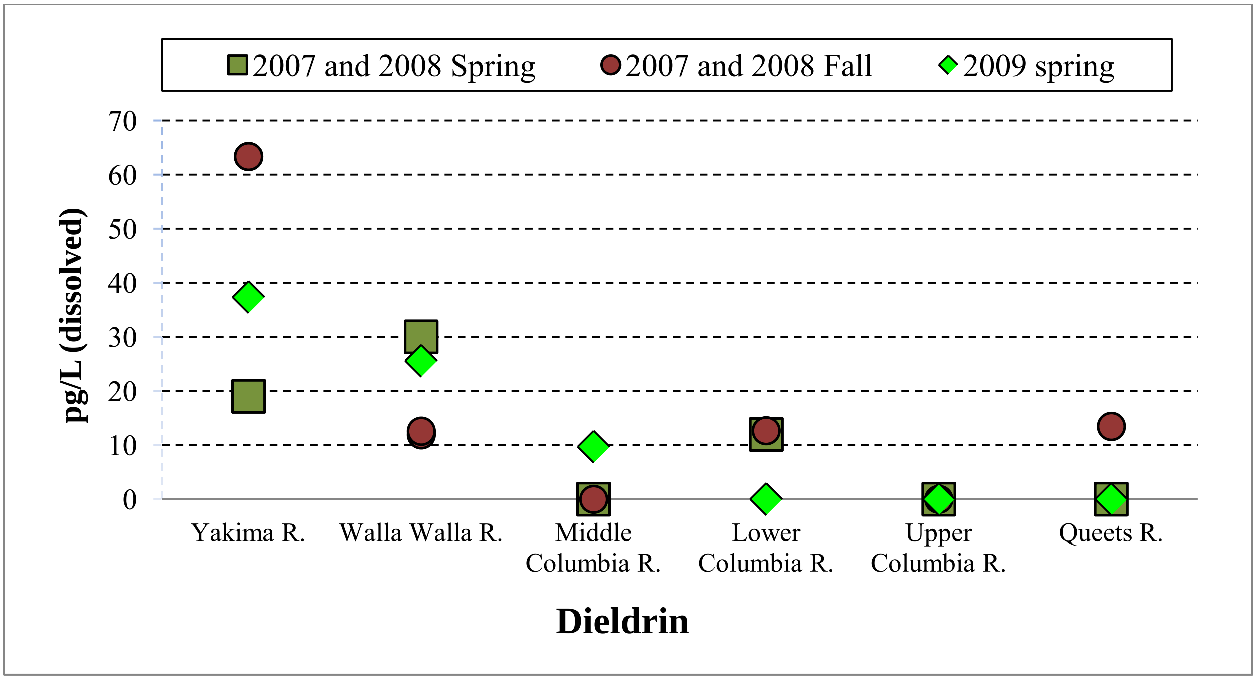

Figure 6. Estimated Dissolved Concentrations of Dieldrin in 2007, 2008, and 2009 Spring and Fall.

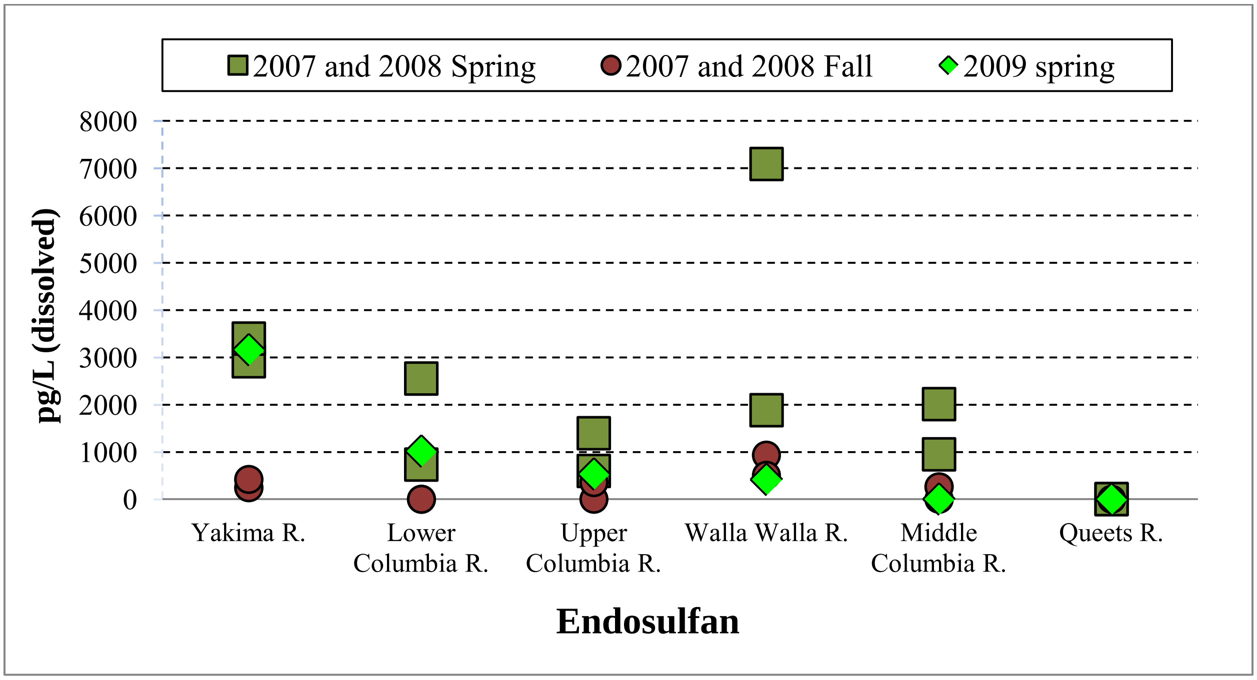

Figure 7. Estimated Dissolved Concentrations of Endosulfan in 2007, 2008, and 2009 Spring and Fall.

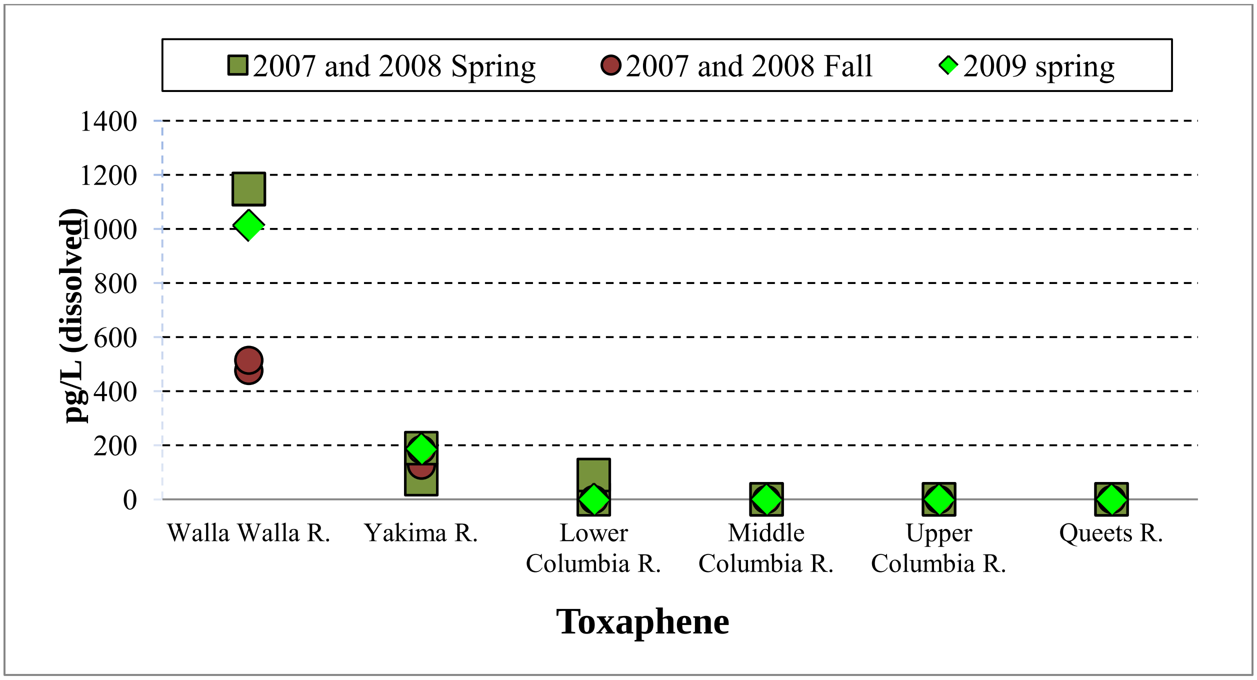

Figure 8. Estimated Dissolved Concentrations of Toxaphene in 2007, 2008, and 2009 Spring and Fall.

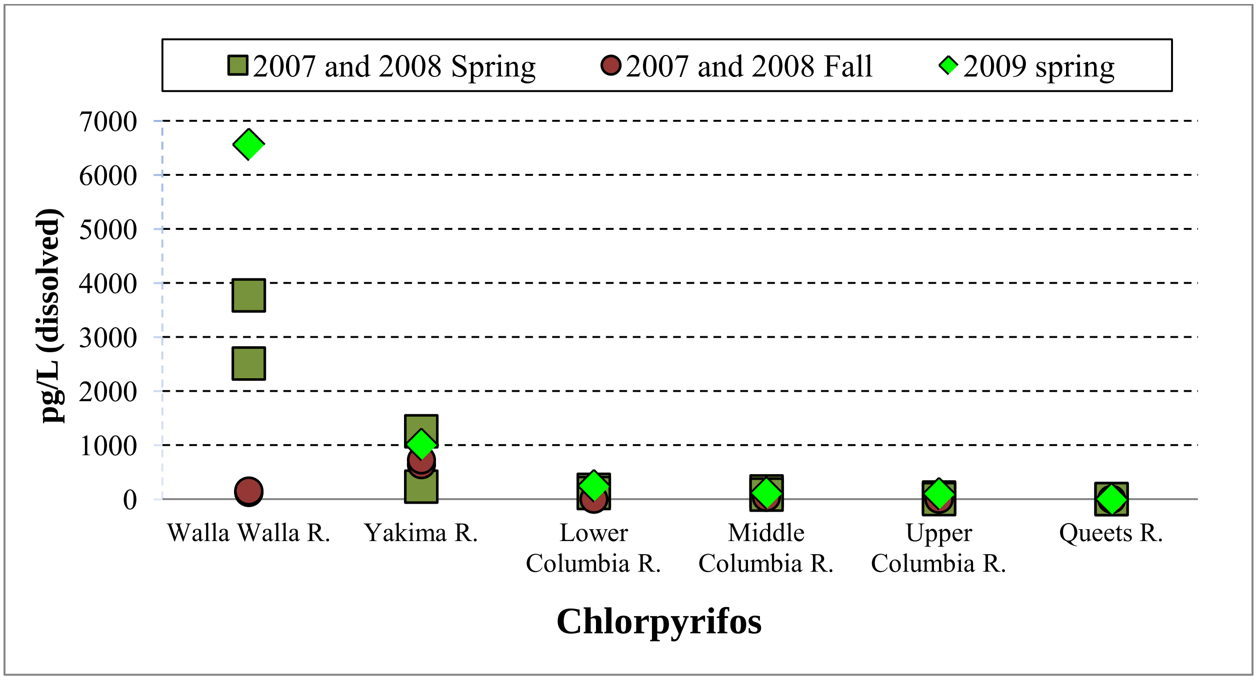

Figure 9. Estimated Dissolved Concentrations of Chlorpyrifos in 2007, 2008, and 2009 Spring and Fall.

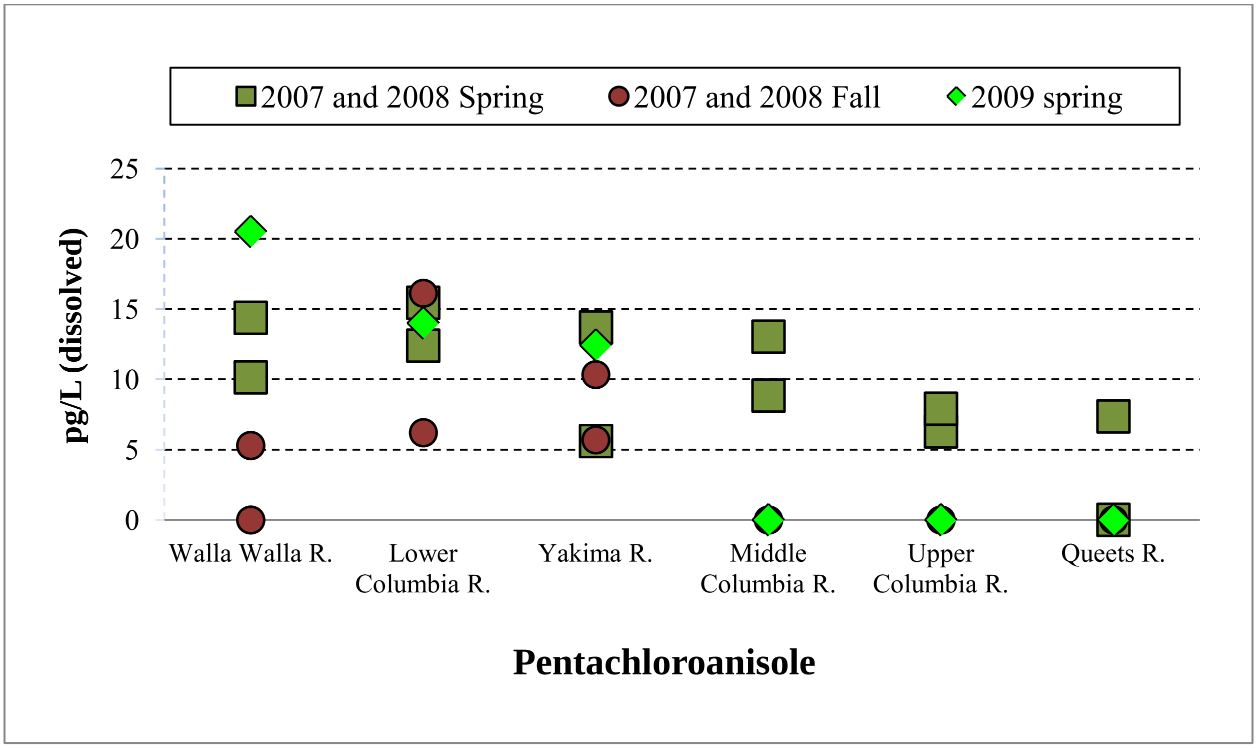

Figure 10. Estimated Dissolved Concentrations of Pentachloroanisole in 2007, 2008, and 2009 Spring and Fall.

Chlorinated Pesticides (CPs)

Highest concentrations of T-DDT in 2009 were found in the Walla Walla, Yakima, and Upper Columbia Rivers. DDT compounds were not detected in the Queets Rivers. These findings are similar to those in 2007 and 2008. An exception was found in the Middle Columbia River, which had lower levels of T-DDT in 2009 (22 pg/L) compared to the spring of 2007 and 2008 (73 and 130 pg/L respectively). T-DDT ranged from 22 – 260 pg/L in 2009 compared to 61 – 230 pg/L and 43 – 340 pg/L in 2008 and 2007 respectively in these rivers (Walla Walla, Yakima, Lower Columbia, Middle Columbia, and Upper Columbia).

The levels of toxaphene, dieldrin, chlorpyrifos, and endosulfan in 2009 were within the ranges found in previous years except for one result of 6600 pg/L of chlorpyrifos in the Walla Walla River. Table 10 shows the range of concentrations for these CPs from all sites during the past three years. The highest concentration of a pesticide was in 2008, where endosulfan in the Walla Walla River was reported at 13000 pg/L. The Walla Walla River site is flanked by agricultural land use; these apparent spikes in endosulfan may reflect application of these pesticides. Year-to-year comparisons are difficult for current-use pesticides such as endosulfan and chlorpyrifos.

Similar concentration levels were reported for pentachloroanisole ranging from 12 – 20 pg/L for the six waterbodies sampled in 2009 as compared to previous years. Twelve waterbodies were sampled in 2007 and 2008 with concentrations ranging from 5.6 – 37 pg/L collectively.

Table 9. Range of Toxaphene, Dieldrin, Chlorpyrifos, and Endosulfan (pg/L, dissolved) among All Sites for 2007, 2008, and 2009.

Chemical	2007	2008	2009[a]
Toxaphene	91 - 1150	130 - 1100	98 - 1000
Dieldrin	11 - 71	11 - 60	11 - 37
Chlorpyrifos	36 - 3800	29 - 2500	99 - 6600
Endosulfan	270 - 3400	240 – 13000	220 - 3200

a. In 2009, sampled only 6 of the 12 original sites for CPs in the spring only.

PCBs

PCBs were detected at all sites as in 2007 and 2008. In decreasing order, the Lower Columbia, Spokane (downstream at Nine Mile Dam), and Yakima Rivers had the highest concentrations in the 2009 spring samples. These were followed by Lake Washington and Spokane River (upstream near the Idaho border). Although both Spokane River locations showed elevated total PCBs, the levels were highest downstream at the Nine Mile Dam location.

The Lower Columbia and Spokane Rivers (at Nine Mile Dam) matched the findings for 2007 and 2008, but the Middle Columbia River had lower levels of PCBs in 2009. Higher PCB concentrations were found in the fall for the Upper and Middle Columbia River in 2007 and 2008. Seasonal differences between PCB concentrations at these sites may be influenced by reservoir or water-control effects as discussed in the report for the 2008 results (Sandvik, 2010b).

PCB-011 was found to be a major congener contributor (greater than 7% to over 20%) to total PCBs in the Lower and Middle Columbia, Spokane, and Yakima Rivers for all three years, which may also help explain their elevated PCB levels. Recent studies are reporting PCB-011 to be a global pollutant from inadvertent production of pigments or dyes (Dingfei and Hornbuckle, 2010; Muñoz, 2007; Rodenburg et al., 2010).

PBDEs

PBDEs were detected at all of the 2009 sites except for the Queets River. Low levels of PBDEs were seen in the Queets River sample but were attributed to background contamination (i.e., these detections could not be blank-corrected). Therefore, the results were considered nondetected at that level.

Concentrations of PBDEs in the Spokane River continue to be the highest in the state. The highest concentrations have been reported in the fall and are greater than ten times higher than other sites (Sandvik, 2009b; 2010b; Johnson et al., 2006; Furl et al., 2010). Although the PBDE levels in the Spokane River were lower upstream near the border, they were still generally above levels reported at other sites from previous years (Table 9).

Table 10. Range of PBDE Concentrations (pg/L, dissolved) in the Spokane River Compared to Other Sites for 2007, 2008, and 2009.

Location	2007	2008	2009
Spokane R. at Nine Mile Dam	180	20 - 220	69 - 240
Spokane R. near Idaho Border	not sampled	not sampled	33
Other Sites	0.9 - 65[a]	2.2 - 18	4.2 - 35

a. Only 2 out of 12 sites in 2007 had levels above 33 pg/L: the Yakima R. at 65 pg/L and Lake Washington at 39 pg/L.

Since 2007, only two sites had PBDE levels above the Spokane River border site: the Yakima River and Lake Washington in 2007 with 65 pg/L and 39 pg/L respectively. The Yakima River site in the spring of 2009 had nearly the same level of total PBDEs (35 pg/L) as the Spokane border site (33 pg/L) in the fall of 2009. At these lower levels (< 50 pg/L), it may be difficult to sort our real differences from background levels.

PAHs

PAHs were detected at all sites in 2009 and 2008. Total PAH ranged from 130 – 5300 pg/L in 2009 compared to 11 - 6500 pg/L in 2008. The urban sites of Lake Washington, the Spokane River, and the Lower Columbia River had the highest total PAH (Figure 11). These same sites were among the top in 2008, which included the Snohomish and Duwamish Rivers that were not sampled in 2009. The Queets River had the lowest concentrations of PAHs in both 2008 and 2009, which reflect the Queets River's remote location in the Olympic National Forest near the Pacific Coast.

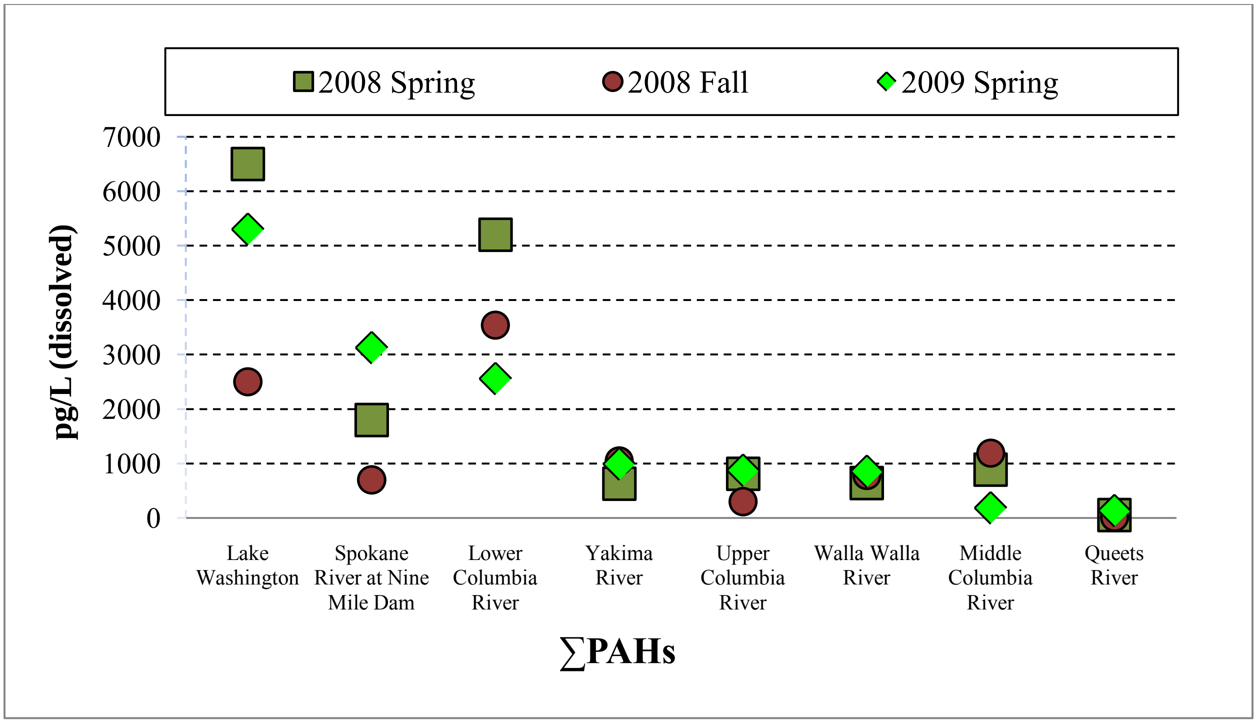

Figure 11. Estimated Dissolved Concentrations of Total PAH in 2008 and 2009 Spring and Fall.

LPAH were the dominant hydrocarbons in most samples for 2008 and 2009. They constituted 63% (in 2008) and 71% (in 2009) of the total PAH concentration based on an average of all sites. LPAH may be derived from slow, long-term, moderate temperatures (petrogenic) and associated with petroleum whereas HPAH are generated mainly by high temperature combustion (pyrogenic) and associated with grass, wood, and coal combustion. In 2008, the main source of PAH observed in these waterbodies appears to be processes related to petroleum combustion and moderate temperature combustion. LPAH tend to degrade more easily than HPAH. Therefore, an abundance of LPAH may indicate ongoing sources verses historical contamination.

Comparison with Water Quality Standards

Federal and state agencies and tribes adopt water quality criteria to protect designated uses such as public water supplies, protection of fish and wildlife, and recreational or agricultural purposes. Although the focus of this study is to determine contaminant trends, comparing the results with criteria helps put the water quality of the study sites in perspective.

Total chemical concentrations were compared to water quality criteria. The dissolved form is usually considered to be the chemical fraction available for bioconcentration by fish (EPA, 2000). Using the total concentration is a conservative approach for comparing to water quality standards. More importantly, the water quality criteria are framed in terms of the total amount of a chemical. Ecology is reviewing procedures for comparing SPMD results with water quality standards. Total chemical concentrations (Appendix K) were estimated from the dissolved data as described earlier.

The 2009 results were compared to the water quality standards and recommended criteria described below. The criteria for Washington State are regulatory whereas the EPA criteria are current national recommendations (Ecology, 2006a). Neither of these sources includes water quality criteria for total PAH. Ecology typically uses SPMD data to estimate contaminant concentrations in water and evaluate trends. Currently, SPMD data are not used for 303(d) listing purposes or other regulatory actions. Comparison with water quality standards in this report are for comparative purposes only.

Washington State Water Quality Criteria

Chapter 173-201A Washington Administrative Code (WAC) establishes water quality standards for surface waters consistent with the maintenance and protection of uses such as public health, public enjoyment, and aquatic life and wildlife resources. Water quality criteria are designed to provide full protection for these uses.

The federal Clean Water Act requires that the waterbodies that fail to meet (exceed) water quality standards be put on a list (known as the 303(d) list) for development of a water cleanup plan specific for the pollutant causing the problem. The cleanup plan results from a Total Maximum Daily Load (TMDL) study and public involvement process. Ecology uses the TMDL program to control sources of the particular pollutant in order to bring the waterbody back into compliance with the water quality standards. To date, Washington State does not list waterbodies based on SPMD water concentrations.

Washington State's human health-based water quality standards for toxic substances are contained in 40 CFR 131.36, also known as the National Toxics Rule or NTR (EPA, 1992). Criteria for carcinogenic substances are based on a risk level of 10^{-6}. The risk level estimates the number of additional cancer cases that would be caused by long-term exposure to a specific contaminant. At a risk level of 10^{-6}, one person in a million could contract cancer due to long-term exposure to a specific contaminant. These risks are upper-bound estimates, while true risks may be as low as zero. Some chemicals in this study, such as endosulfan and chlorpyrifos, are not carcinogens. These compounds have criteria values below which adverse health effects are expected.

Washington State's aquatic life-based criteria are set at levels that provide full protection of the aquatic-life designated uses found in the standards.

EPA National Recommended Water Quality Criteria

EPA periodically updates their national recommended numeric criteria for human health and aquatic life protection, as required by the Clean Water Act (section 304(a)). These recommended criteria are used by states as they consider updates to their standards, but are not regulatory values unless adopted into state standards and approved by EPA.

Criteria Comparison

Human Health Criteria

Results from this 2009 study were compared to the Washington State water quality standards and EPA recommended criteria for protection of human health and aquatic life. Criteria for protecting human health from the consumption of water and organisms (fish) (Appendix L) were compared to results for total chemical concentrations.

The waterbodies monitored in 2009 met water quality criteria for most of the chemicals of concern. Exceptions included PCBs, toxaphene, and DDE.

Five waterbodies did not meet (exceeded) the Washington State human health criterion (170 pg/L) for total PCBs: the Lower Columbia, Yakima, Walla Walla, and Spokane Rivers, and Lake Washington. All sites sampled in 2009 exceeded the EPA national recommended human health criterion (64 pg/L) (Figure 12).

No sites exceeded the Washington State human health criterion for dieldrin (140 pg/L) or the EPA national recommended human health criterion (52 pg/L) (Figure 13).

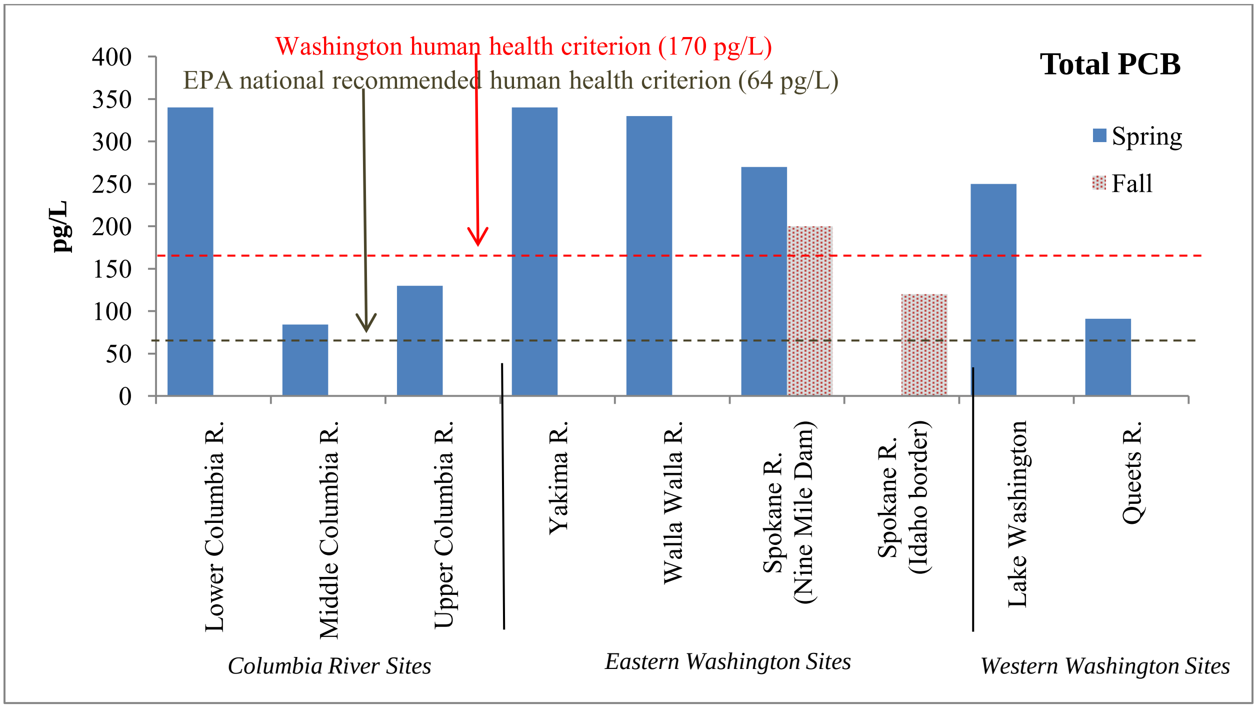

Figure 12. Estimated Total Concentrations of Total PCBs Compared with Washington State and EPA National Human Health Criteria. (nd = not detected.)

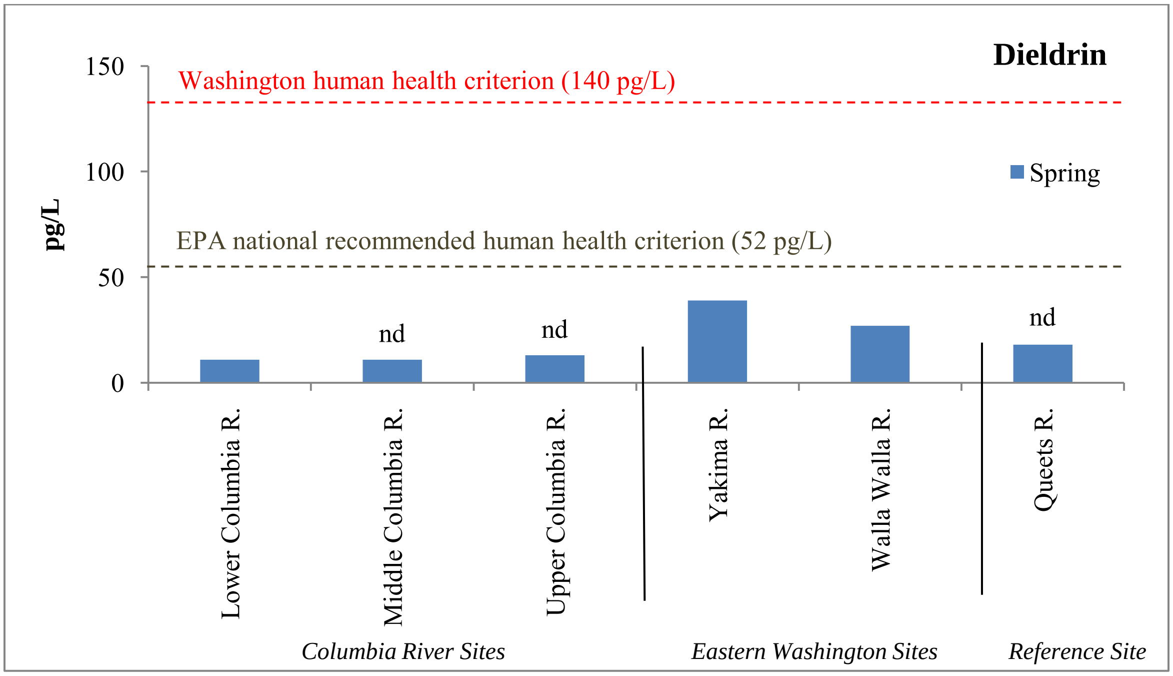

Figure 13. Estimated Total Concentrations of Dieldrin Compared with Washington State and EPA National Human Health Criteria. (nd = not detected.)

The Yakima River exceeded the EPA national recommended human health criterion for dieldrin in the fall of 2008 with a concentration of 65 pg/L. Johnson et al. (2010) suggested a potential groundwater contribution based on dieldrin having an inverse relationship with flow in the Yakima River. He found the Lower Yakima River consistently exceeded criteria in the second half of the irrigation season during low flows (last half of June through August). Since CPs were sampled only in the spring of 2009, the period for maximum concentrations of dieldrin was missed.

The Walla Walla River exceeded the Washington State human health criterion of 730 pg/L and the EPA national recommended human health criterion (280 pg/L) for toxaphene with a concentration of 1100 pg/L (Figure 14).

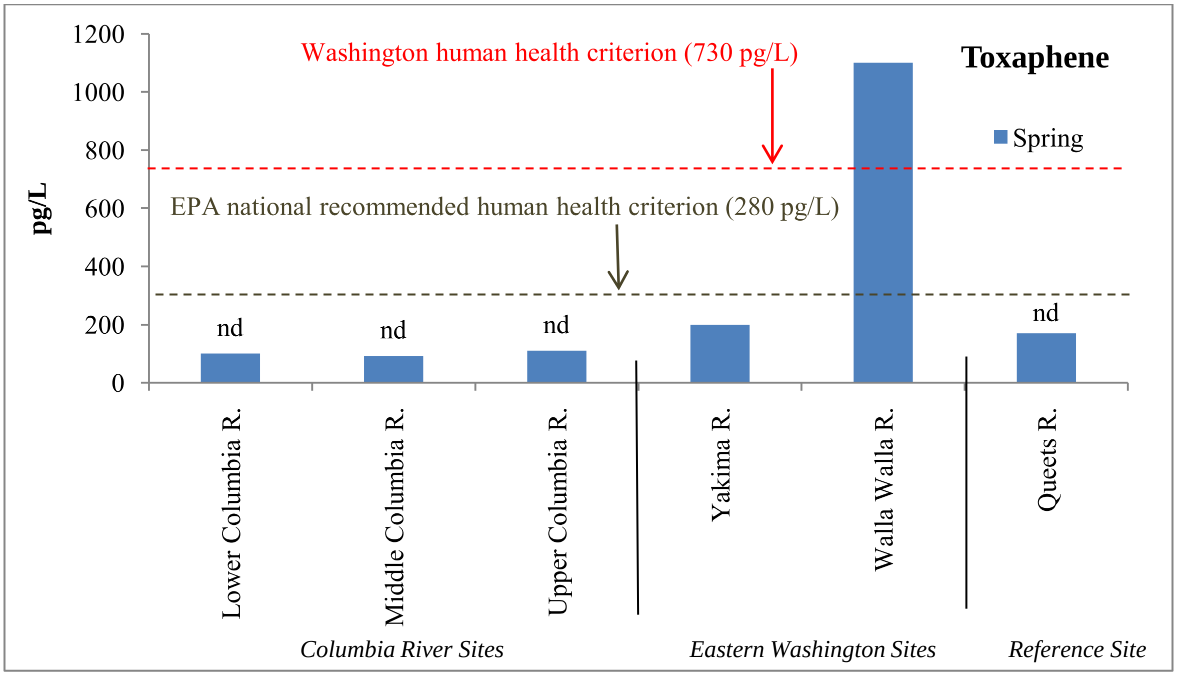

Figure 14. Estimated Total Concentrations of Toxaphene Compared with Washington State and EPA National Human Health Criteria. (nd = not detected.)

Toxaphene concentrations in the Walla Walla River in 2007 and 2008 (spring) were 1200 pg/L each exceeding both criteria, and 500 and 550 pg/L respectively in the fall exceeding the EPA national recommended human health criterion. Pine Creek, a tributary, was found to be a major source of the toxaphene concentration found in the Walla Walla River (Johnson et al., 2004). Currently, Ecology is conducting a study looking for toxaphene in treated lakes and agricultural streams including the Walla Walla River and some suspected tributaries (Johnson, 2010).

No levels of DDT or metabolites exceeded Washington State human health criterion (590 pg/L). The Walla Walla and Yakima Rivers exceeded EPA national recommended human health criterion (220 pg/L) for DDE with concentrations of 470 and 390 pg/L respectively (Figure 15).

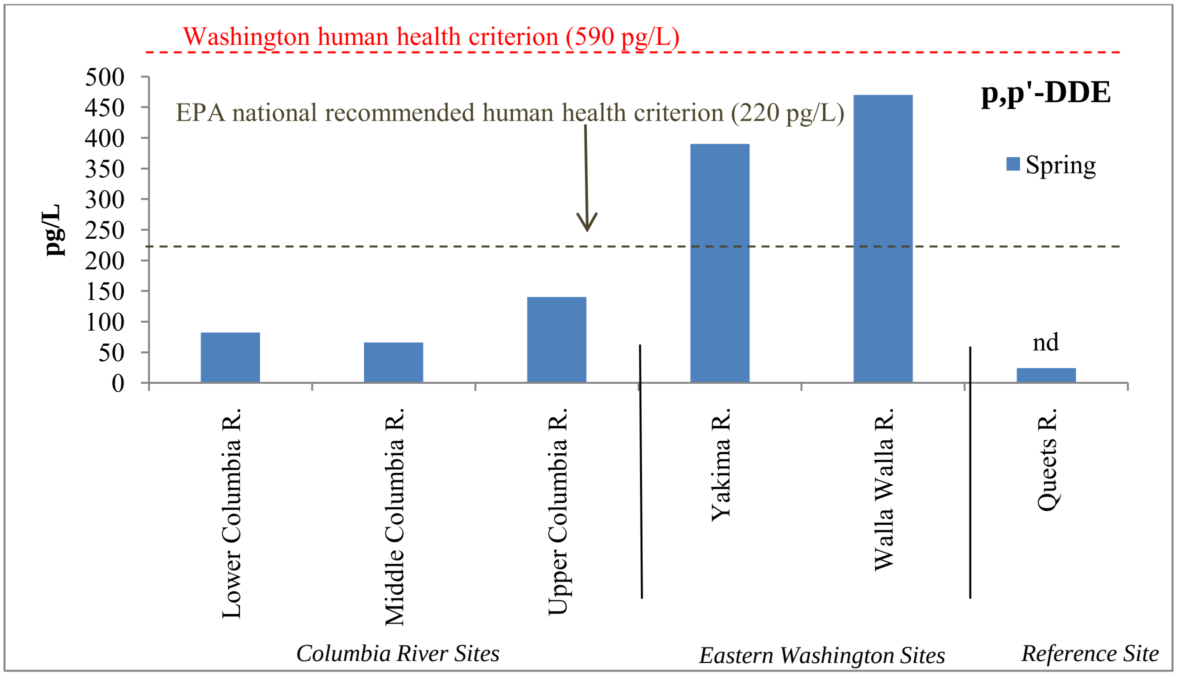

Figure 15. Estimated Total Concentrations of Total DDE Compared with Washington State and EPA National Human Health Criteria. (nd = not detected.)

High concentrations of DDE were found in 2007 and 2008 for the Walla Walla River ranging from 170 – 360 pg/L and in the Yakima River ranging from 140 – 380 pg/L. Decreasing trends of DDT and metabolites have been reported in the Yakima River based on fish and whole water data, but sporadic exceedances still occur in the mainstem (Johnson et al., 2010).

Aquatic Life Criteria

Concentrations of toxaphene and T-DDT were compared with Washington State and EPA acute and chronic aquatic life criteria. No results were above the acute criteria. The Walla Walla River did not meet (exceeded) Washington State chronic aquatic life criterion for toxaphene (200 pg/L) in 2009 (1100 pg/L). The Yakima River was just at the criterion level at 200 pg/L. This agrees with results from 2007 and 2008 finding toxaphene concentrations at or above the aquatic life criterion in the Walla Walla and Yakima Rivers (Sandvik, 2009b, 2010b; Johnson et al., 2010).

No sites had T-DDT that exceeded aquatic life criteria (1000 pg/L) in 2009. Both DDE and DDD appear to be the major contributors to T-DDT. DDT compounds break down very slowly and remain in agricultural soils a long time. The breakdown products (DDE and DDD) are often found in surface water.

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Conclusions

In the spring of 2009, Ecology sampled seven Washington rivers and one urban lake for PCBs and PAHs. These sites were a subset of the same 12 sites monitored previously in 2007 and 2008. Five of these seven waterbodies were also analyzed for CPs and six were analyzed for PBDE flame retardants. In the fall of 2009, the Spokane River was sampled in two locations for PCBs and PBDEs while other sites were suspended from sampling to reserve time to access additional QC sampling.

Results in this report are presented for the third year (2009) of this long-term PBT Trends Study. Comparisons are made among sampling sites, 2007 and 2008 data results, and water quality criteria. Additional quality control results are summarized in the report with a detailed discussion in Part 2.

Major findings from the 2009 monitoring are:

- A total of 12 field samples were analyzed in 2009 (10 in the spring and 2 in the fall). Many of the results were similar to results from 2007 and 2008.
- PCBs, CPs, and PAHs were detected in all samples analyzed for those chemicals. PBDE flame retardants were detected in 89% of the samples analyzed.
- In general, the frequency of detection was higher for most CPs in 2009 than in 2007 or 2008. This can be explained, in part, by the fact that CPs were analyzed only in the spring of 2009. Previous results show CPs to be found more often and at higher concentrations in the spring.
- The highest concentrations for individual chemicals were found in the following waterbodies:
    - T-DDT in the Walla Walla River.
    - Total PCBs in the Lower Columbia River.
    - Dieldrin in the Yakima River.
    - Toxaphene in the Walla Walla River.
    - Chlorpyrifos in the Walla Walla River.
    - Endosulfan in the Yakima River.
    - PBDEs in the Spokane River.
    - Total PAH in Lake Washington.
- Several waterbodies, listed below, did not meet (exceeded) Washington State criteria or EPA national recommended water quality criteria for the protection of human health and aquatic life. It should be noted that Ecology typically uses SPMD data to estimate contaminant concentrations in water and evaluate trends. Currently, SPMD data are not used for 303(d) listing purposes or other direct regulatory actions. Comparison with water quality standards in this report are for comparative purposes only.

  - Five waterbodies exceeded the Washington human health criterion for PCBs: Lower Columbia, Yakima, Walla Walla, and Spokane Rivers, and Lake Washington.
  - All sites exceeded the EPA national recommended human health criterion for total PCBs.
  - No waterbodies exceeded the Washington or EPA criteria for dieldrin.
  - Toxaphene in the Walla Walla River exceeded the Washington human health criteria, EPA national recommended human health criteria, or Washington aquatic life criteria.
  - The Walla Walla and Yakima Rivers exceeded the EPA national recommended human health criterion for DDE.

- SPMDs continue to be a good monitoring tool for certain chemicals. Yet their use requires a substantial effort to ensure useful data. Quality assurance and quality control practices need particular attention, especially for PCBs, PBDEs, and PAHs.

- The ability to measure spatial or temporal trends with SPMDs at many sites is compromised because contaminant levels at some sites are low relative to the noise in the sampling system.

Recommendations

Recommendations from the third year (2009) of this long-term program are:

- Discontinue trend monitoring for PAHs because (1) the levels found indicate low environmental risk, (2) levels of sample contamination will likely compromise the ability to detect trends over time, and (3) resources could be more effectively used elsewhere in this project.

- Continue monitoring at sites that are most promising for trend detection or represent important water basins. Sites that are promising for trend detection would have results that are 5 to 10 times higher than the reporting limit, which would be approximately equal to 50-100 times higher than levels measured in blanks. Sites recommended for continued monitoring are:
    - Spokane River at Nine Mile for PBDEs and PCBs.
    - Yakima River for PCBs and CPs.
    - Walla Walla River for CPs.
    - Lower Columbia River for PBDEs, PCBs, and CPs.
    - Queets River for PBDEs, PCBs, and CPs.

- Suspend monitoring at all sites after the fifth year of monitoring (2011) to allow time to review results from all years, test for trends, evaluate effects of corrective actions, analyze changes in SPMD methodology, and recommend future actions.

- Conduct a separate focus study for PCB-011 to identify the sources near monitoring sites that have elevated levels of this congener.

- Consider using SPMDs for screening waterbodies for CPs, PBDEs, and PCBs. SPMDs could be used as a tool for locating sources within a waterbody or for identifying the time of highest concentrations. Screening could include certain sites (e.g., Lake Washington) every few years for contaminants of concern such as PBDEs. Sites with appropriate characteristics could then be added to a long-term trend monitoring effort.

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PART 2: RESULTS FROM ADDITIONAL QUALITY CONTROL SAMPLING

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Introduction

The 2009 spring monitoring effort added additional quality control (QC) procedures and samples to help address concerns about the levels of contamination found in various blanks[3] in this PBT Trends Study and other Ecology studies using SPMDs.

The main concerns were:

- High levels of contamination in field blanks confounded interpretation of data.
- Variability in blanks was poorly understood, which reduced confidence in results obtained from blank-corrections procedures.
- The sources and magnitude of contamination in blanks were undefined making it unclear where corrective actions should be pursued.
- The low levels of contamination with certain chemicals have raised questions about the ability of this monitoring effort to actually detect trends over time or among sites.

The additional QC work began to address concerns and improve the quality of the data for this PBT Trends Study and other SPMD projects. The use of SPMDs requires project leaders to adopt QC practices that have traditionally been done within laboratories, such as ensuring various blanks are used and checking the cleanliness of reagents used in sample preparation and analysis.

Results from the extra QC efforts were designed to better:

- Identify sources of contamination and reduce levels.
- Improve information about sampling variability.
- Define the limits at which trends could be detected.
- Guide the practice of blank-correcting sample results.
- Use monitoring resources wisely.

This section (Part 2) includes results from the additional QC work done in the spring of 2009. All results are from residues (concentrations found in extracts from SPMDs after dialysis and GPC).

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[3] Blanks are prepared and analyzed along with the samples to measure the response of the analytical system to the analyte at a theoretical concentration of zero. Blanks detect bias due to contamination.

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Laboratory Case Narrative Summary

MEL prepared written case narratives assessing the quality of the data collected during the 2009 spring and fall sampling events. CPs, PBDEs, PCB congeners, and PAHs were analyzed in the spring samples, but only PBDEs and PCB congeners were analyzed in the fall samples. Case narratives are available upon request. An overview of the data quality for the 2009 PBT Trends Study is summarized below.

All samples were prepared and analyzed within the methods holding times for the various parameters with one exception for TSS. That result was qualified as an estimate. Analytical laboratory methods blanks showed no significant contamination for any of the chemicals analyzed, but a few PCBs were found at low levels in the method blanks. The few samples that were less than 10 times those levels were QC samples. These were qualified as nondetects. Most QC procedures and corresponding samples fell within acceptable limits. Exceptions were qualified as estimates and are briefly discussed below.

Pesticides

All calibration checks were within QC limits for detected analytes except for dacthal in three samples: 0906043-05, 0906043-06, and 0906043-13. Dacthal results for those samples were qualified as estimates.

Positive qualitative identification was made for all pesticide analytes with a few exceptions in the 2009 spring samples. The exceptions were qualified as estimates (for RPDs > 40%) or nondetects (for chromatographic interferences). Qualified samples included:

- 0906043-03 for 4,4'-DDT.
- 0906043-05 for 4,4'-DDT and endosulfan I.
- 0906043-06 for g-BHC, 2,4'-DDD, 2,4'-DDT, 4,4'-DDT, endosulfan I, cis-chlordane, dieldrin, and trans-nonachlor.
- 0906043-13 for 4,4'-DDT and endosulfan II.

Concentrations of technical chlordane and toxaphene were determined using 3 – 10 of the most prominent homologs for averaging and comparing to a commercial standard. Components that appear to be masked by interference are avoided in this calculation. Because these analytes undergo processes in the environment that degrade (or "weather") these components, the pattern of these contaminants rarely show the same ratios as the commercial standards. Therefore, if the homologs exceeded 40% RPD, the results were reported as estimated concentrations (J). One detected technical chlordane result and two detected toxaphene results were qualified as estimates.

PBDEs

Both spring and fall samples had excellent QA results for PBDEs. Only one spring sample (0906043-25) required qualification (J) because the surrogate recovery was below the acceptable range of 50% - 150%. During the preparation of the sample at MEL, an unknown amount of sample was lost which is reflected in the low recovery. Another spring sample (0906043-01) had an unknown amount of sample lost during preparation although surrogate recovery was acceptable. Results in these samples were qualified as estimates: J for detected results and UJ for nondetected results.

PCBs

All calibration standards for PCBs were within the QC limits with a few exceptions. However, as the Ongoing Precision and Recovery blank (OPR) recoveries were acceptable, no action was taken. Also, all internal standard recoveries were within the QC limits with two exceptions in one spring sample (0906043-04). Associated congeners PCB-001 and PCB-002 (some of the most volatile ones) were qualified as tentatively identified estimates (NJ) in this sample.

Each congener reported as detected met the isotopic abundance ratio and retention time criteria for positive identification with several exceptions. These exceptions have been qualified to reflect tentative identification, and the associated numerical value represents its approximate concentration: qualified NJ. The values reported for these congeners were not included in the totals for the corresponding homolog.

A number of congeners were qualified as estimates (J) because the concentration was below the lowest calibration standard. Also, low levels of certain target compounds were detected in the laboratory blanks. All corresponding concentrations were qualified as nondetects with an estimated reporting limit (UJ) because the values were below the reporting limit (0.02 ng/sample) and less than 10 times that of the corresponding method blank.

PAHs

All calibration checks for PAHs were within QC limit with a few exceptions. All affected results were qualified UJ nondetects since there were no detections.

No target compounds were found in an in-house method blank except a small amount of benzo(a)anthracene. This blank does not appropriately apply to the samples, therefore no qualifiers were added.

Two isotopically labeled compounds (acenaphthylene-d8 and pyrene-d10) were added after recovery from the field but prior to dialysis as surrogates. Recoveries of acenaphthylene-d8 were consistently lower and often less than 50%. Recovery of the acenaphthylene-d8 in the in-house blanks and laboratory control samples (LCS) were above 50%. Low recoveries of the surrogate compound could indicate losses during dialysis and GPC cleanups. Where the pyrene-d10 recovery was acceptable, no qualifiers were added. Four samples had low pyrene-d10 recoveries: 0906043-01, 0906043-02, 0906043-23, and 0906043-25. The low recoveries may be explained through some lab accidents which caused some loss of the sample. All results for these samples were qualified as estimates (J) if detected and UJ if not detected.

Field Quality Control Samples

SPMDs

All SPMDs were retrieved for the 2009 spring and fall sampling events. One SPMD sampler (0906043-15) was compromised in the field due to high spring runoff washing the sampler up on the bank presenting it partially out of the water. SPMDs were checked for presence midway (two weeks) during the deployment period.

TidbiTs

Onset StowAway TidbiTs™ were used to measure water and air temperature during deployment. These data were used to determine if the SPMDs remained submerged during deployment. One TidbiT™ was attached to the top of each SPMD canister that was in the water and another TidbiT™ was secured out of the water nearby. Each TidbiT™ was programmed to record temperature every two minutes. The date and time of deployment and retrieval was recorded to capture the exact monitoring period.

Upon retrieval, the data were downloaded and charted for comparing the water and air temperatures. If the SPMDs were out of the water during the sample periods, a spike in water temperature appeared on the graph and followed the same temperature values as the air during the time period the SPMDs were exposed to the air.

Six TidbiTs™ displayed error messages, but data were recovered for all but one. This pertained to the Lower Columbia replicate sample. There is high confidence that the sampler was not compromised due to air exposure because this sampling site is located out of public access, the samplers were deployed at least 7 to 10 feet underwater, and results seem similar to the temperature taken manually. These results have been qualified as estimates (see discussion for *Field Replicate Samples*).

All results used in this study were from SPMDs that remained submerged during the 2009 monitoring period. Mean water temperatures can be found in Appendix D.

Matrix Spike Recoveries

All compound recoveries fell within the acceptable 50% - 150% recovery limits with several exceptions in the 2009 spring samples: one PBDE (209 congener) and several PAHs. There were no field samples with detected PBDE-209 so no results were qualified based on the low PBDE-209 recovery. Low PAH recoveries included naphthalene (32%), 2-methylnaphthalene (43%), acenaphthylene (32%), acenaphthene (35%), dibenzo(a,h)anthracene (41%), fluorene (33%), phenanthrene (47%), anthracene (47%), and pyrene (44%). No sample results were qualified based on the matrix spike recoveries. These samples are considered more like a spiked blank than a true matrix spike because they are spiked at the processing laboratory, not the analytical laboratory.

PRC and Surrogate Recoveries

The PRC and surrogate recoveries were within acceptable ranges: 20 – 80% recovery for PRCs and 25 – 150% for surrogates with a few exceptions. PRC and surrogate solutions were analyzed to verify concentrations. PRC concentrations matched documentations whereas the surrogate concentrations were twice as high as were reported by the manufacturing laboratory. The 2009 recoveries for surrogates were based on the surrogate solution analysis; 2 times the concentrations documented for spiking.

PRCs with low K_{ow} values, such as PCB-004, typically dissipate faster than the more hydrophobic PRCs. Recoveries for PCB-004 ranged from 16% to 79% which were considered acceptable since other PRCs were within range. High PRCs were reported for several spring samples. These were found in two field samples (090604304 and 090604314, Queets River and Spokane River replicate respectively) and QC samples for the field-trip extended-air blanks, the Day0-dialysis blanks, and a single FreshDay0-dialysis blank. The Queets River PRCs were considered acceptable since the other PRCs were within range. The Spokane River replicate PRCs were considered acceptable since the Spokane River field sample had nearly the same values (RPDs ≤7%) (Appendix G). Laboratory staff reported some minute loss in GPC collection from part of the Spokane River replicate sample which may explain some of the differences.

Five surrogates for PCBs (PCB-014) were recovered above the 150% limit in the 2009 fall field and QC samples. A few surrogates for PAHs were outside the recovery limits as mentioned in the above QC section for PAHs. These were considered acceptable since the other surrogates were within range.

Field Replicate Samples

Field sample replicates were deployed to estimate total variability in the field and laboratory. In the spring, three locations had field replicates: the Lower Columbia, Spokane, and Yakima Rivers. No replicates were deployed in the fall because of the small sample size and sample area: sampled two locations in the Spokane River only.

Each replicate contained five SPMD membranes (like the field sample) and was deployed beside the sample within a few feet. Unfortunately, the field replicate in the Yakima River (sample number 0906043-015) was compromised as mentioned above. Results from the other two replicate samples are listed in Appendix G.

The replicates showed good precision in most cases with over 80% of the residue results having RPDs of 20% or less. PCB residue results showed excellent precision for individual congeners in both field replicates with greater than 80% having RPDs of 20% or less collectively. The congeners with RPDs greater than 20% were detected near or below the detection limit (0.02 ng/sample). As a result, precision was good for total PCB congeners (< 5% RPD) for both replicates.

Lower variability was observed in the Spokane River replicates compared to the Lower Columbia River replicates for PBDE and PAH residues. More than 75% of the detected PBDE and PAH results for the Spokane River had RPDs 20% or less whereas less than 30% of detected results had RPDs ≤20% for the Lower Columbia River. CPs showed a similar pattern of variability for the Lower Columbia River replicates with only 25% of the detected results having ≤20% RPDs. CPs were not analyzed in the Spokane River samples.

The higher variability in the Lower Columbia River replicate samples may be due to a lab accident in which the sample container was broke but was reported with no estimated loss of sample extract. The higher variability appears to show evidence of some loss of extract. All results were qualified as estimates for CPs, PBDEs, and PAHs. PCB congeners were analyzed from a separate vial of extract that was not broken. PCB congener results confirm low variability with more than 90% RPDs ≤20% for this site.

Variability in the estimated water concentration between replicates reflects the differences in PRC recoveries and has been shown to follow a similar pattern as the residue results (Sandvik, 2010b). These are not reported for 2009 because the overall RPDs for CPs, PBDE, PCB, and PAH residue concentrations remain generally within 30% or better.

Field and Processing Blanks

The additional QC work in the 2009 spring monitoring effort focused on blanks in order to better understand the sources, magnitude, and variability of contamination of the sampling system. Results from laboratory QC procedures show that analytical procedures used with sample extracts introduce little contamination. Varied blanks were often contaminated by PBDEs, PCBs, and PAHs during manufacturing and processing the SPMDs. No CPs were detected in the field or in processing blanks.

Background

For most monitoring programs, the signal from the environment would ideally be far larger than any "noise" from the measurement system. The threshold at which one distinguishes a true "signal" from the environment is often characterized as a given signal-to-noise ratio. This ratio is often 5 or 10: i.e., if the level of noise in the system exceeds 10% of the value of the signal from the environment or sample, the signal from the environment is deemed unreliable. In the case of a sample, such a result may be qualified as a non-detect.

The level of noise in some measurement systems can be determined from sample blanks. In this monitoring effort, the noise in the measurement system for some analytes accounts for a large proportion of the result of the sample taken from the environment.

Figures 16 and 17 show that the results for individual samples are highly influenced by contamination in the sampling system. For PBDEs, contamination in the field blank consistently accounts for about 50%-80% of the sample value, and in some cases far exceeds the sample value shown. The picture is similar for PCBs (Figure 17) and PAHs (not shown). For most sample events shown in these figures, a single field blank was used.

These high levels of blank contamination have been a concern in Ecology projects using SPMDs for some time. The variability of contamination in blanks is also a concern because the variability can affect the quality of results depending on how blank-correction is performed. Ecology SPMD projects have typically used a single field-trip blank to characterize contamination encountered in the field during deployment and retrieval of SPMDs. The implied assumption has been that a single blank at any one site adequately represents the level of contamination from air during deployment and retrieval at all sites. This assumption was explored by using additional field-trip blanks during the 2009 spring sampling event.

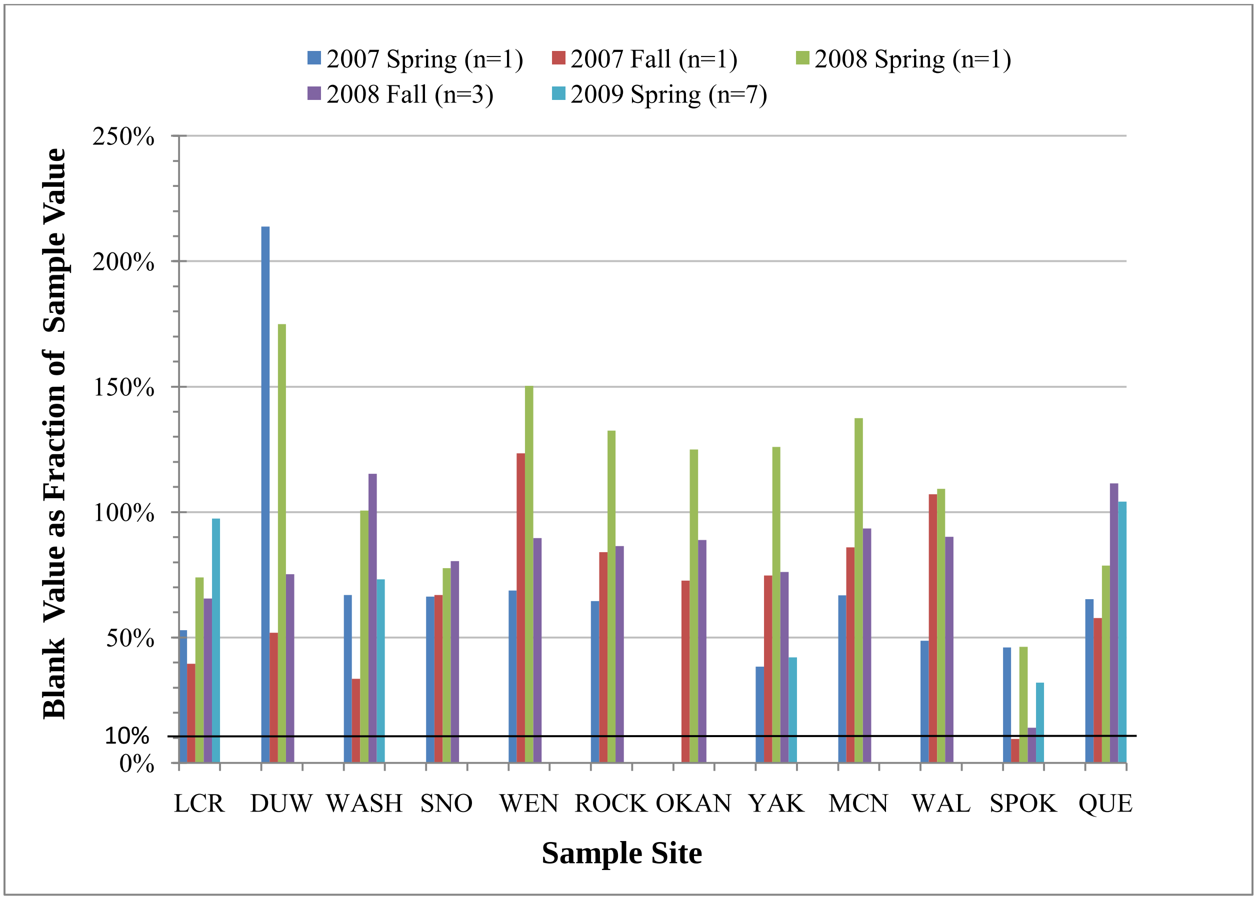


Figure 16. Level of Field Blank Contamination as Fraction of Sample Result for Total PBDE (five sample events).

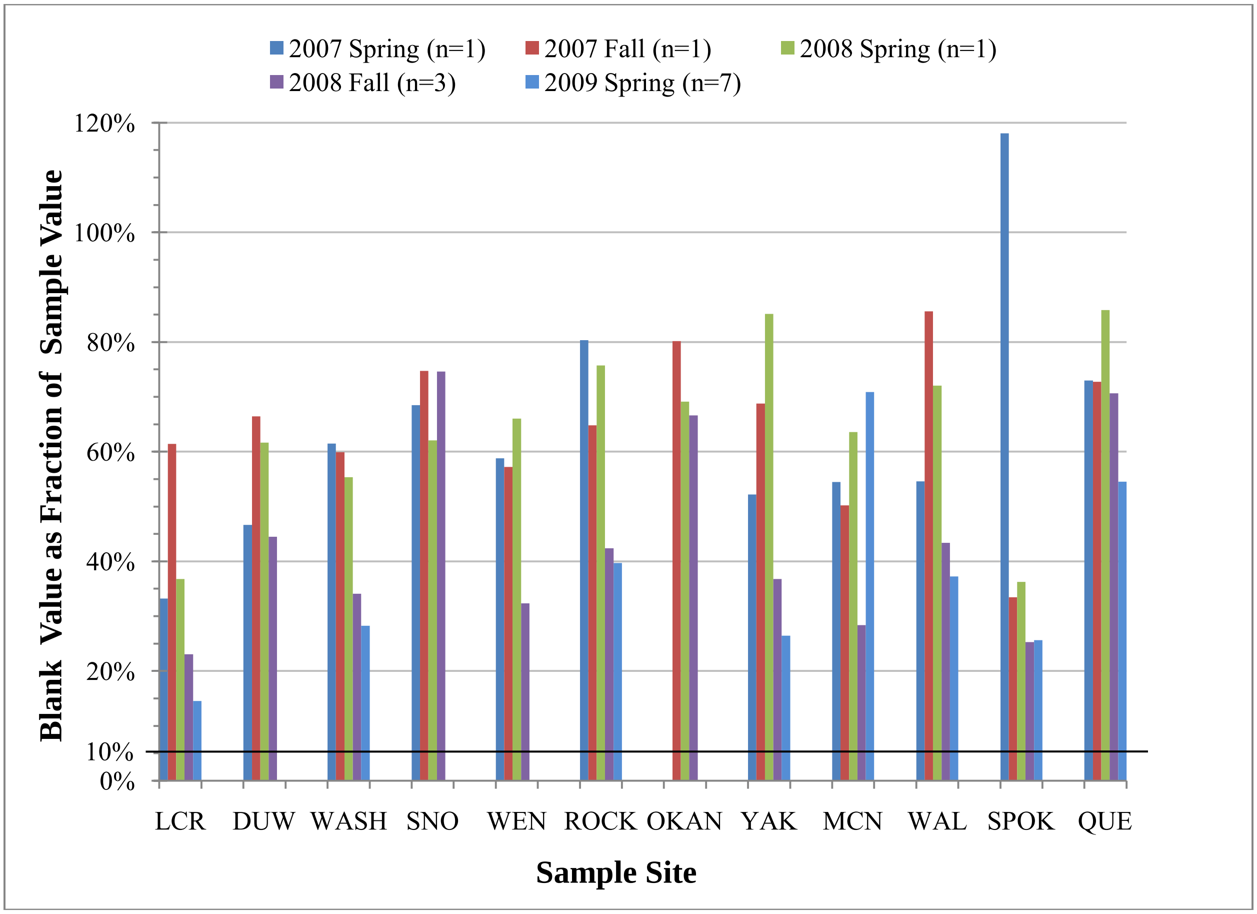


Figure 17. Level of Field Blank Contamination as Fraction of Sample Result for Total PCBs (five sample events).

Figures 18-20 show results from the 2009 spring sampling where individual field blanks were done at seven of the eight sampling sites. The level of contamination remains to be a large contributor to the sample results. For PBDEs and PAHs, the value in the blank accounts for more than 50% of the sample result for most samples. Contamination for PCBs is less pronounced than for PBDEs, yet remains around 30-60% of the sample value.

The levels of contamination in the field-trip blanks vary across sites which suggests that blank-correction using any single blank (the common practice) could give varied results, depending on which blank was used. With PBDEs for example, blank-correcting the Queets River sample using the blank results from the Walla Walla River would yield a negative value for total PBDE. The use of blank-correction procedures outlined in the EPA 1600 method series as described earlier in this report avoids the derivation of negative results. Blank correction is also discussed later in this report.

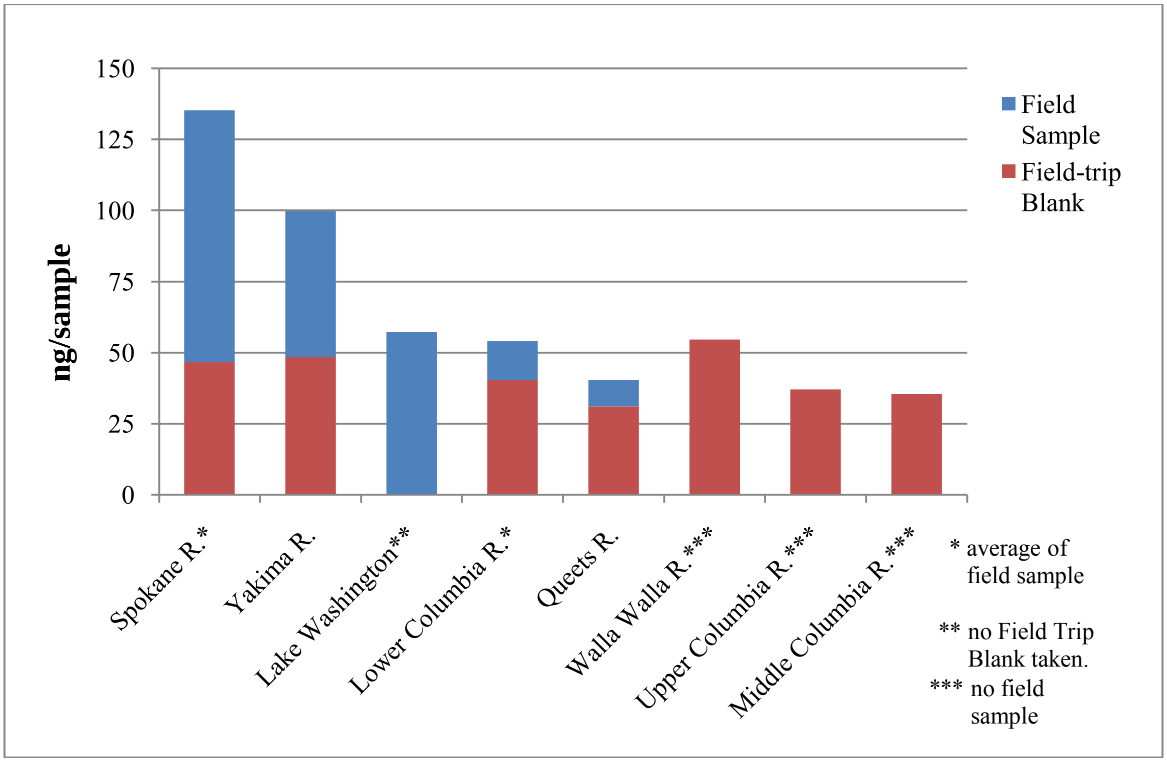


Figure 18. Amount of Contamination in Total PBDE Results from 2009 Spring Sampling.

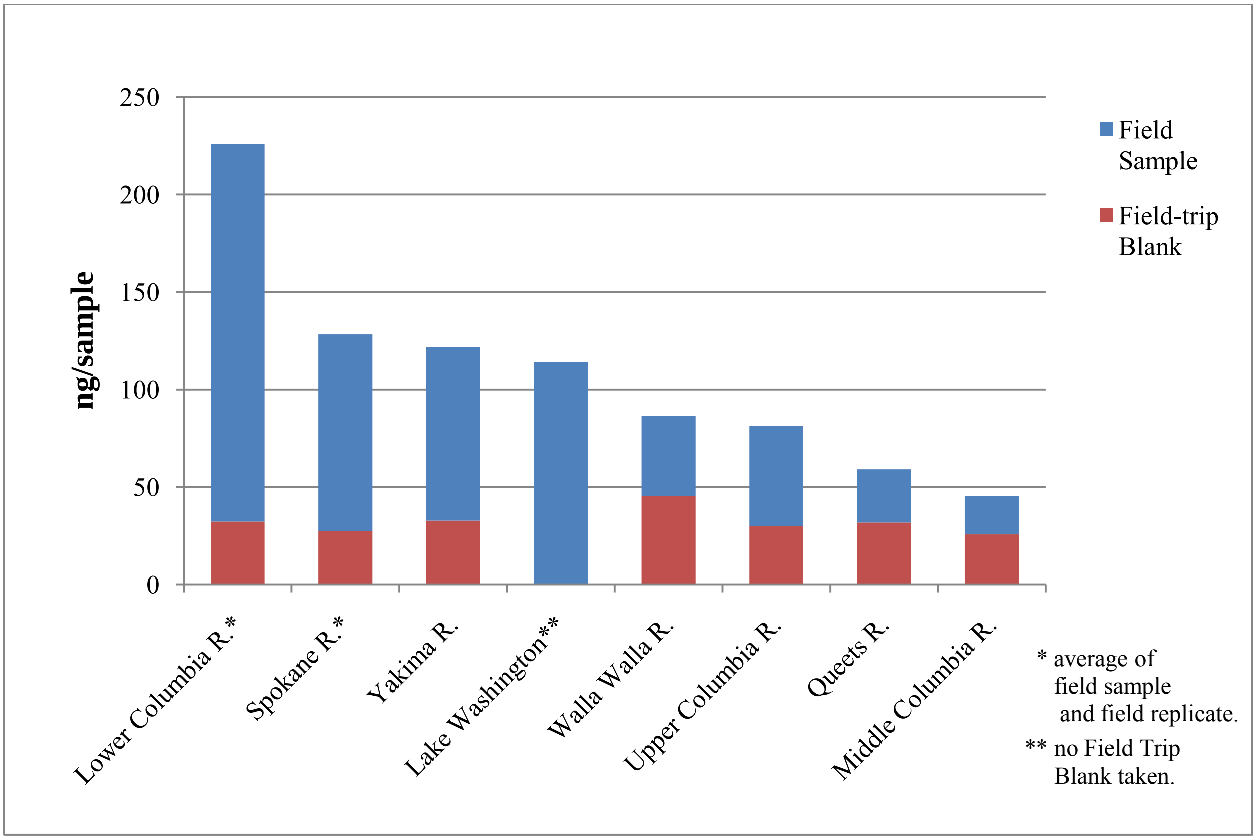


Figure 19. Amount of Contamination in Total PCB Results from 2009 Spring Sampling.

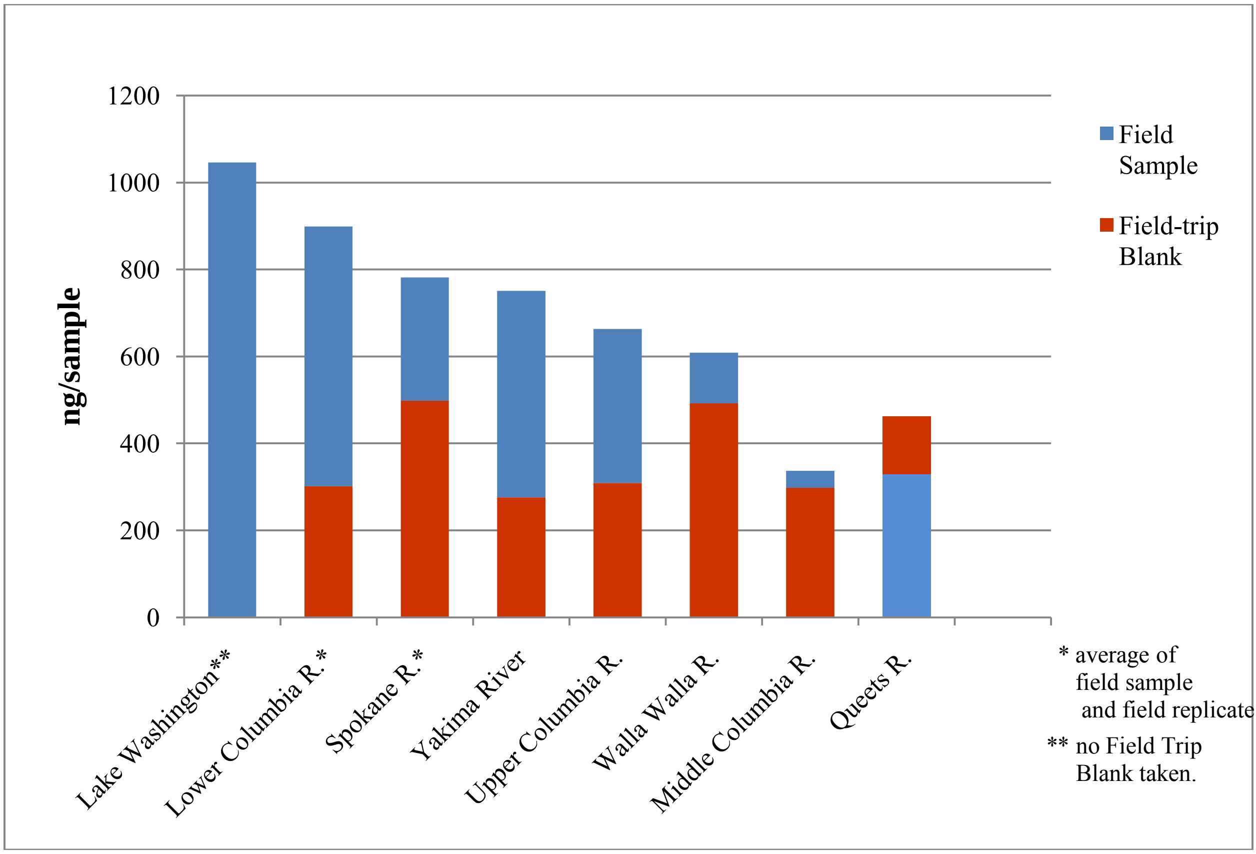


Figure 20. Amount of Contamination in Total PAH Results from 2009 Spring Sampling.

Description of Blanks

Blanks Used in 2009 Sampling

Table 11 shows the various blanks analyzed during the 2009 spring sample event. Each of these blanks consisted of five SPMD membranes, except for the FreshDay0 blanks (one SPMD membrane each) and the solvent GPC blanks (solvent only).

Table 11. Types of Blanks Analyzed during the 2009 Spring Sampling.

Blanks	Total Amount	Chemicals Analyzed			
		Pesticides	PBDEs	PAHs	PCB Congeners
Field-trip Blank[1]	7	7	7	7	7
Field-trip Extended-air Blank[2]	3	2	2	2	3
Day0-dialysis Blank	3	3	3	3	3
FreshDay0 Blank	3	0	3	3	3
Dialysis No Spiked Blank	2	0	2	2	2
Solvent-GPC Blank	1	0	0	0	1

[1] Sites Sampled: Lower, Middle, and Upper Columbia River; Queets, Yakima, Walla Walla, and Spokane Rivers.
[2] Sites sampled: Queets, Yakima, and Spokane Rivers. Because of a laboratory accident, the Spokane River extract was analyzed for PCB congeners only.

The field-trip blanks corresponded to each site sampled in the spring except Lake Washington. The three field-trip extended-air blanks were taken at sites thought most likely (Yakima and Spokane Rivers) and least likely (Queets River) to contaminate the blanks or samples through exposure to air. Field-trip blanks were exposed to ambient air for two minutes, whereas the field-trip extended-air blanks were exposed for 20 minutes (10 times longer). Both trip blank types were analyzed for all the chemicals of interest with one exception. The Spokane River field-trip extended-air blank was analyzed for PCBs only because a lab accident precluded analyses for other analytes.

The 2009 fall sampling event used fewer blanks: a single field-trip, Day0-dialysis, and FreshDay0 blank were analyzed. The fall field-trip blank was taken at the downstream location on the Spokane River (Nine Mile Dam). Analyses for this site were limited to PBDEs and PCBs.

Field Handling of Field-trip Blanks

How well the field-trip blank represents sample contamination from air during deployment and retrieval is another concern for data quality. The current practice has the field blank treated differently from how the samples are handled:

- For field samples, individual membranes (usually five) are mounted on "spider arrays" which facilitates handling and allows their full surface area to be exposed to the sample medium (water and air). The spider arrays with membranes are stored in an argon-filled can. At the sampling site, the spider arrays with membranes are removed from the transport can, transferred to the sampling canister, and the canister then placed underwater. This process takes 30 to 120 seconds, which is the time sample membranes are exposed to air.

- For field-trip blanks, the membranes lay at the bottom of their own argon-filled can. The membranes are usually in a rolled-up state and are not mounted on spider arrays. To mimic the exposure of the sample, the lid on the can is simply removed and then replaced after a certain amount of time: the argon-bathed membranes are not removed from the can nor are the full surface areas of the membranes exposed to the argon-air mixture. Argon is about 40% denser than air.

Because of limited resources, evaluation for potential differences between handling the field blank using the current practice and handling the field blank the same way that the samples are handled was not done. The use of blanks in other measurement systems typically has the blank handled the same way as the sample.

Types of Blanks Used for Contamination Assessment

Table 12 shows the types of blanks used to assess contamination during the 2009 spring sampling. All steps in the use of SPMDs, from manufacture to final lab analyses, are represented in the left-hand columns from top to bottom. Each step is a potential contributor of contamination to each blank if indicated by an “X”.

Various blanks were then used to identify the sources and magnitude of contamination in some steps of using SPMDs. For example, contamination from air exposure during deployment/ retrieval at a particular site would be the difference between the values for the field-trip blank for that site and the Day0-dialysis blank. Other blanks give a more direct characterization, such as the SOL-GPC blank which is the solvent used for dialysis and also goes through the GPC clean-up process. The estimated magnitudes of contamination should be considered semi-quantitative because of variability in contamination.

Results from the various blanks were used to identify the major sources and magnitudes of contamination in SPMDs. Figure 21 shows that the steps involved in manufacturing, storage, dialysis, and GPC account for the majority of contamination for PBDEs, PCBs, and PAHs. Contamination from the spiking processes was a larger contributor for PBDEs than for PCBs and PAHs. Contamination from transport and ambient air at the time of deployment and retrieval was minor for PBDE and PCB yet accounted for 15-20% of total contamination for PAHs. For PCBs, it appears that some PCBs actually move out of the membranes while the membranes are exposed to air during deployment and retrieval.

Table 12. Potential Sources of Contamination in SPMDs and Sample Blanks used during 2009 Spring Sampling.

Potential Sources and Locations of Contamination = X		Name of Blank				
		Field (Trip)	Day0-dialysis	Fresh Day0	Dialysis No Spiked	Solvent-GPC**
Fabrication	manufacturing (mfg)	X	X	X	X	
	spiking: PRCs	X	X			
	storage at EST	X	X	X	X	
Field Storage & Transport	storage + transport to field	X				
	air exposure: deployment *	X				
	storage + transport to-from field *	X				
	air exposure: retrieval *	X				
	storage + transport from field	X				
Post-Field Processing & Extraction	spiking: PRCs			X		
	storage at EST	X	X	X	X	
	spiking: surrogates (CP, PAH, PBDE)	X	X	X		
	dialysis (extraction)	X	X	X	X	X
	GPC	X	X	X	X	X
	extract: storage + transport	X	X	X	X	X
Lab	extract: lab analysis	X	X	X	X	X

* Sample SPMDs are deployed in water for about 28 days at this time.

** The Solvent-GPC blank is a solvent blank that goes through the dialysis and GPC procedures.

Descriptions of Blanks

Field (Trip): field and transport blank.
Day0-dialysis: SPMD fabrication blank.
FreshDay0: SPMD process blank.
Dialysis No Spiked: unspiked SPMD process blank.
Solvent-GPC: unspiked reagent blank; for PCBs only.

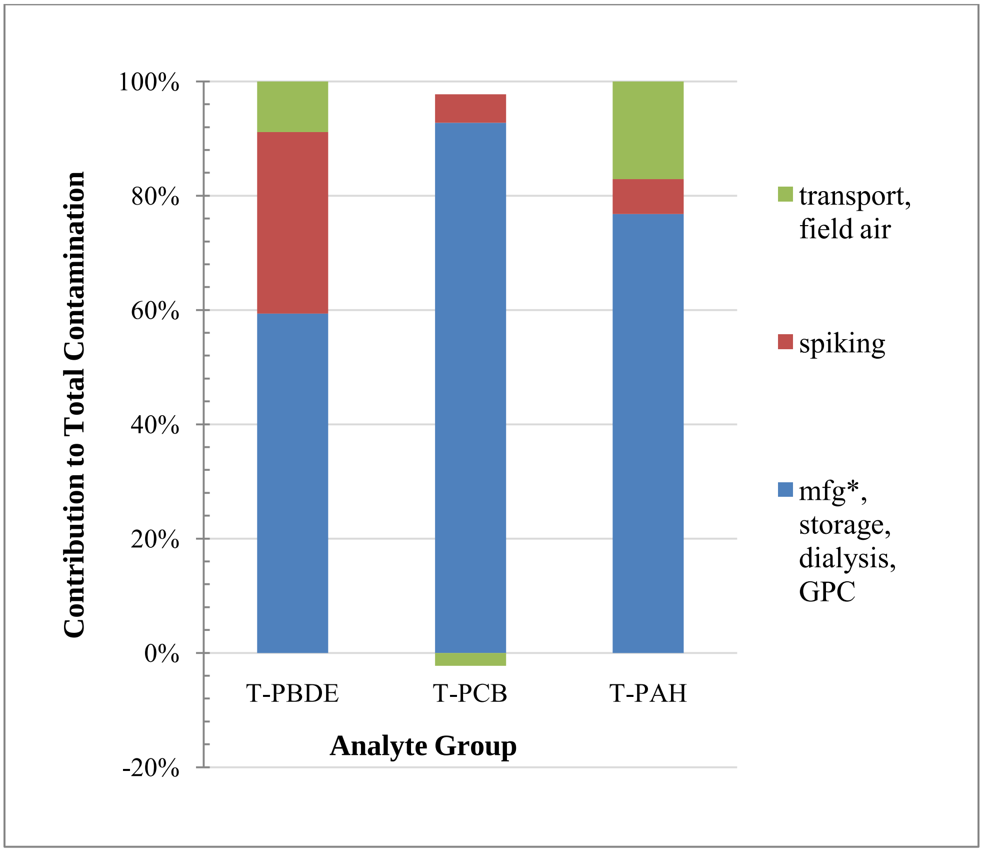


Figure 21. Major Sources of Contamination to SPMDs during 2009 Spring Sampling.
**mfg = manufacturing.*

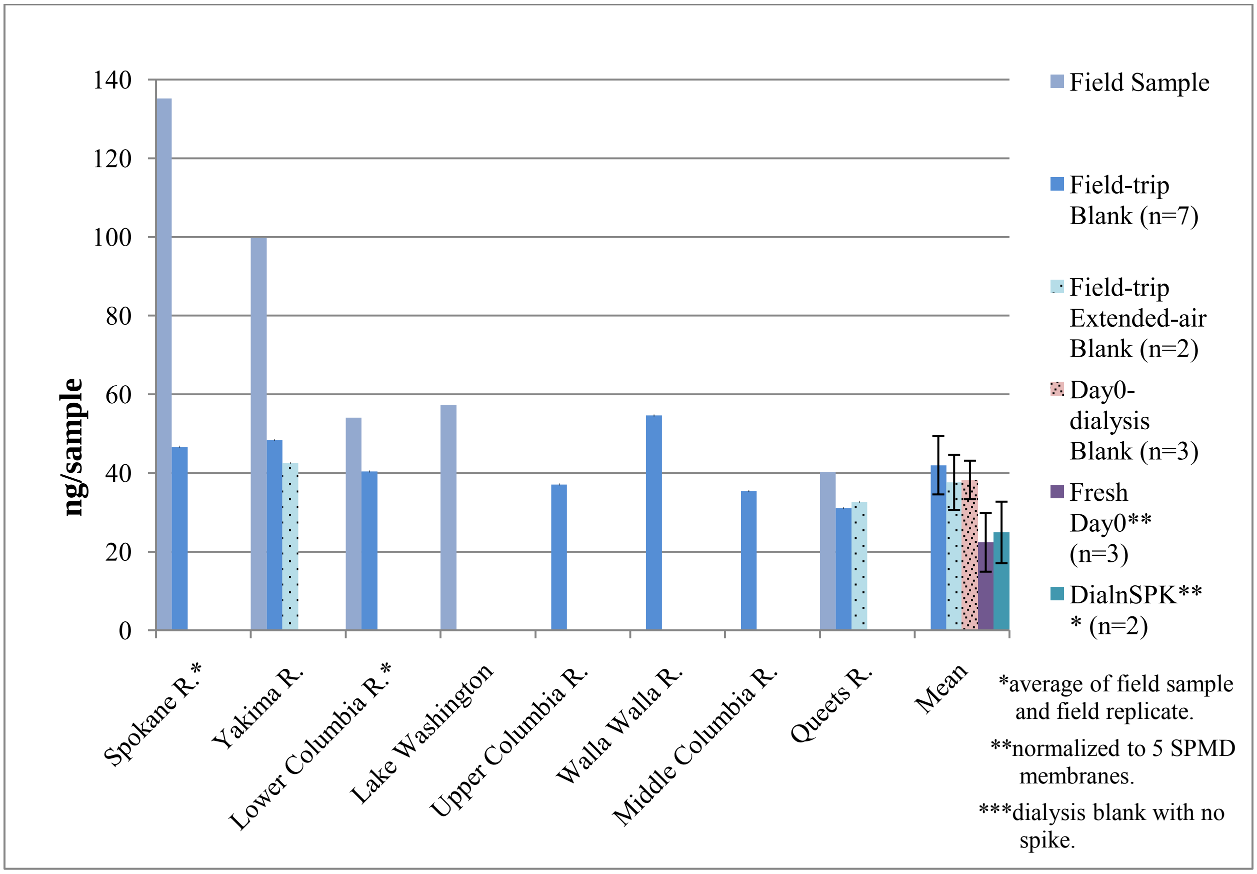
Results from Blanks by Analyte Group

Overall, there were no CPs detected in any blanks, but certain analytes were found in the other chemical groups (PAHs, PBDEs, and PCBs). Comparison was made to blanks from the 2007 and 2008 PBT Trends Studies, and results are discussed below. 2008 and 2009 blank results are comparable because the field and laboratory procedures were similar. Differences to spiking, laboratory, and chemicals analyzed generally resulted in more variability when compared to the 2007 blank results.

PBDEs

Overview

Figure 22 shows total PBDE results for the 2009 spring sample event. It is clear that levels of contamination account for a large proportion of the sample result at each site. Another observation is that the results for the seven field-trip blanks are quite variable. It is not clear whether this variability is due to differences among the air at each site, or is part of the variability within all aspects of SPMD fabrication and processing.



*average of field sample and field replicate.

**normalized to 5 SPMD membranes.

***dialysis blank with no spike.

Figure 22. Total PBDEs in Sample Results and Blanks from 2009 Spring Sampling.

The “noise” in the sampling system for total PBDEs (as represented by field-trip blanks) seems to be around 30-50 ng/sample. This level of noise needs to be considered when using sample results for identifying trends or determining the level of PBDEs in water.

Review of PBDE contamination in blanks from 2007 to 2009 suggests that levels of contamination are somewhat consistent within a sampling period, but less definitive among sampling periods. So the variability of contamination by PBDEs should be defined for each sampling event (e.g., 2010 spring) until more results from blanks are acquired over time.

Levels of Contamination in Different Blanks

Figure 23 shows boxplots which display the range of values for PBDEs from the 2009 spring blanks and the 2008 fall field-trip blanks. The field-trip extended-air, field-trip, and Day0-dialysis blanks from 2009 spring have nearly the same amount of total PBDE in them. It appears that contamination from air during deployment and retrieval is minimal. The lower values for the FreshDay0 and Dialysis No Spike blanks, in comparison to the other blanks, suggest contamination from the storage and spiking processes. In the 2008 fall sampling, three field-trip blanks were done, and the plots for these illustrate the variability from year to year in this blank.

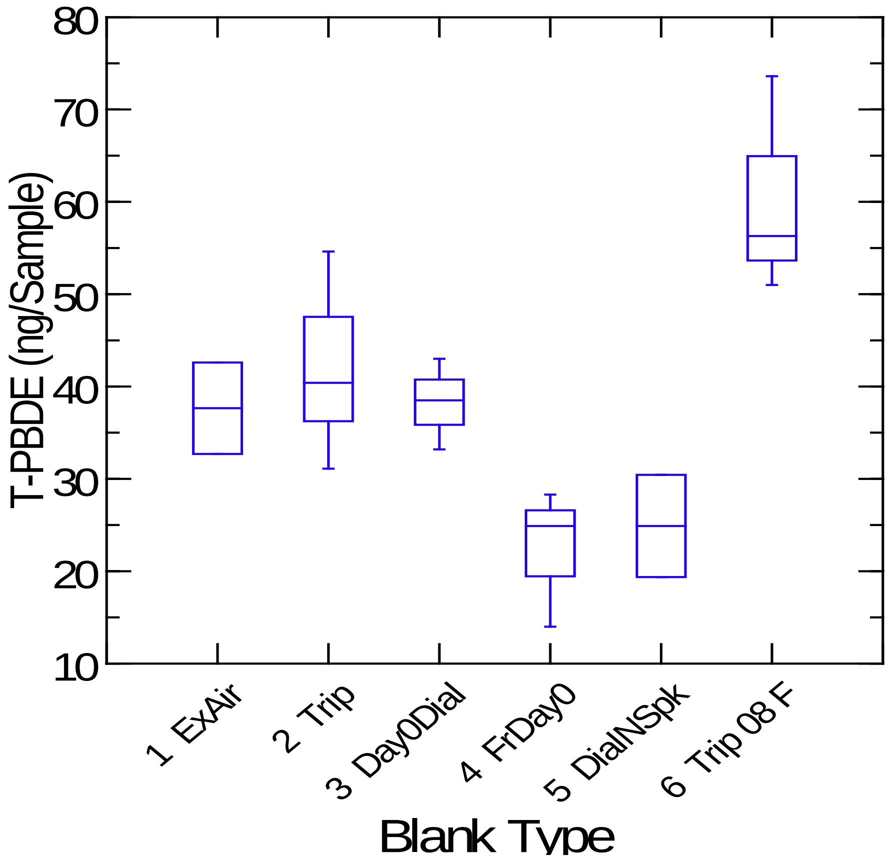


Figure 23. Boxplots of Total PBDE Results from Various 2009 Spring and 2008 Fall Blanks (ng/sample).

ExAir = field-trip extended-air blanks (n=2), Trip=field-trip blanks (n=7),
Day0-Dial = Day0-dialysis blanks (n=3), FrDay0 = FreshDay0 blanks (n=3),
DialNSpk = dialysis blank with no spikes (n=2).

Field-trip Blank verses Day0-dialysis Blank

Figure 24 shows PBDEs in the field-trip and Day0-dialysis blanks for each sample event since 2007. The level of contamination seen in the Day0-dialysis blank for each sample event varies from around 20 ng/sample (2009 fall) to 130 ng/sample (2007 spring). The range for the field-trip blank is smaller.

Figure 24 also shows that neither blank is consistently greater or smaller than the other (e.g., 2009 fall: field-trip > Day0-dialysis; 2008 fall: Day0-dialysis > field-trip). The differences between the two blanks are also inconsistent, sometimes similar (2009 spring) and sometimes very different (2007 and 2008 spring). Yet these apparent differences may not be real because of the high variability results from the blanks. A paired-sample t-test was performed on the six paired results from the project's beginning in 2007 and indicated no difference between results for field-trip and Day0-dialysis blanks (alpha=0.05, P=0.53).

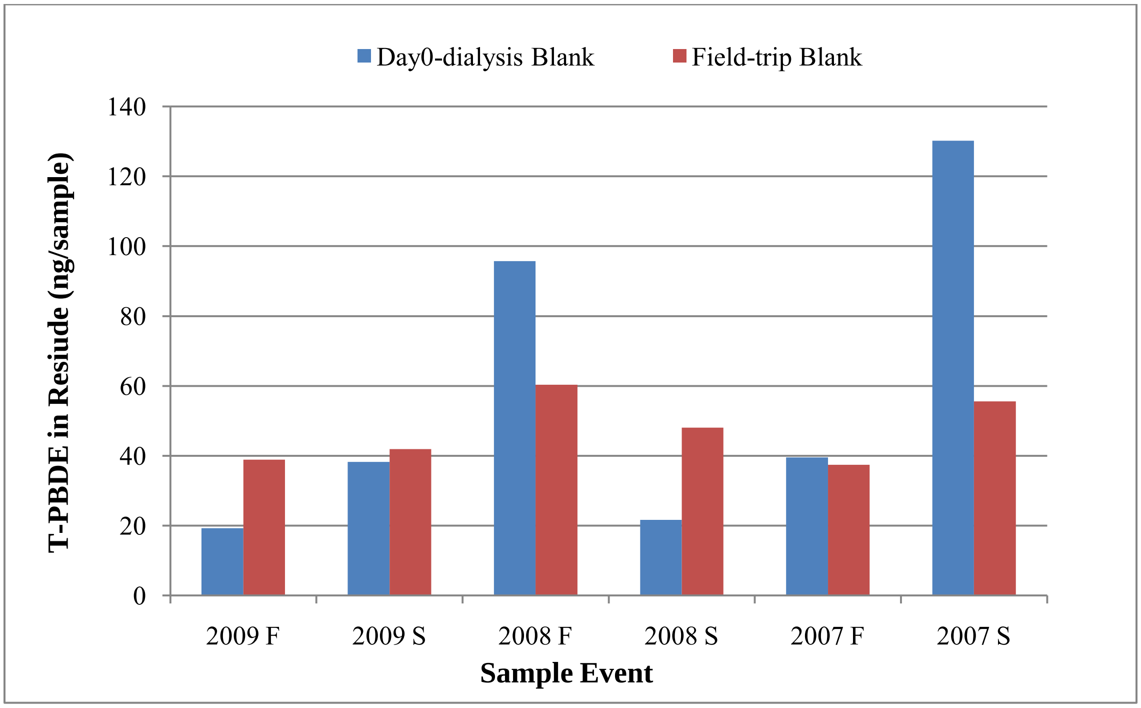


Figure 24. PBDEs in the Field-trip and Day0-dialysis Blanks, 2007 – 2009.
S = spring, F = fall.

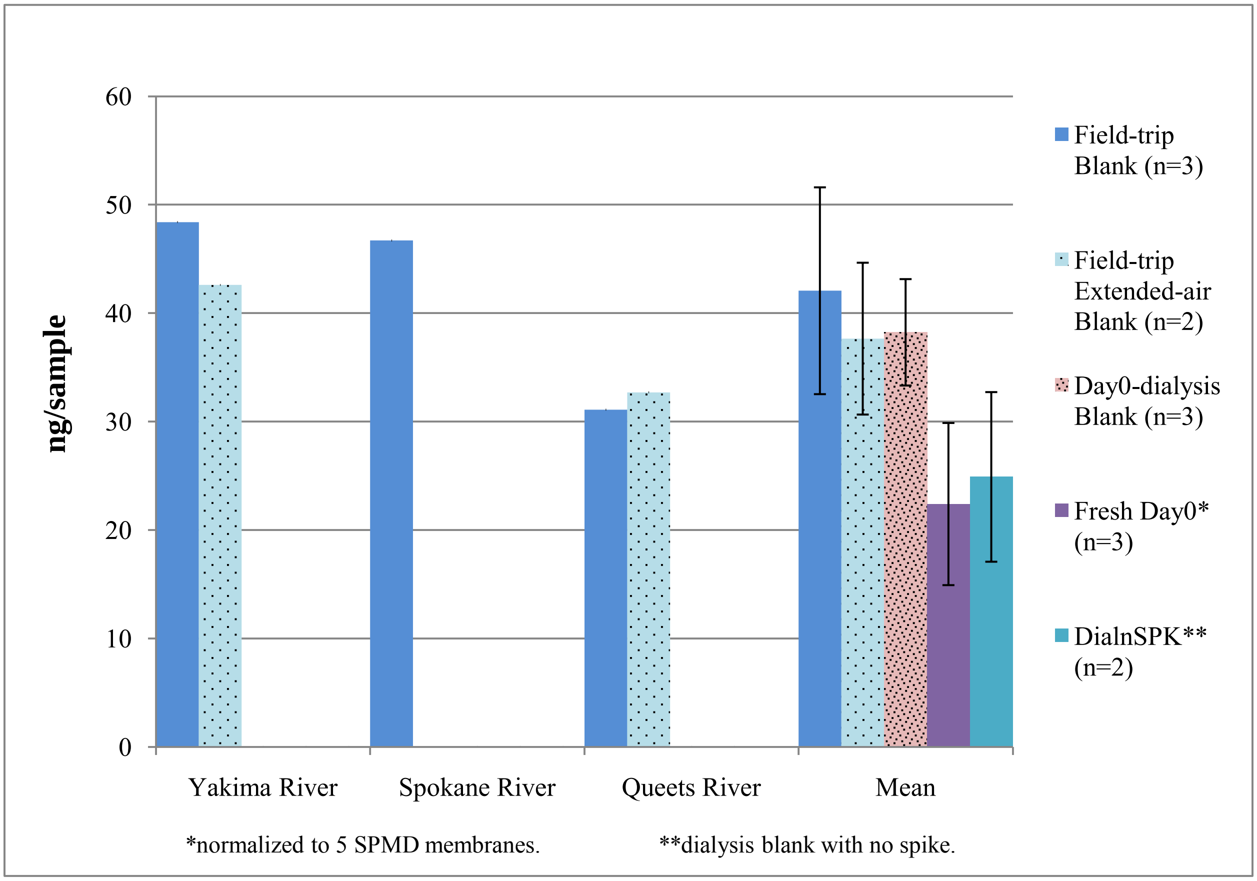
Contamination from air during SPMD deployment and retrieval is likely inconsequential. However, if there is contamination from the air, it may be masked by the variability in the results for the blank samples. The paired-sample test was not very powerful because of the high variability and small sample size.

From Figure 23, it is not clear whether the larger range of results for the trip blanks (versus the range for the Day0-dialysis blanks) represent contamination from air during deployment and retrieval or is simply from a larger variability because there were seven blanks used (versus three blanks used for the Day0-dialysis).

It may be that for PBDEs the use of both field-trip blanks and Day0-dialysis blanks is not necessary. Yet, other factors need to be considered before deciding to discontinue one of these blanks, such as: other target analytes from the sample, how the blank is actually exposed (current practice does not mimic the way samples are exposed), and concerns about high variability.

Field-trip Extended-Air verses Field-trip Blanks

Figure 25 compares results for Total PBDEs among the field-trip blank, field-trip extended-air blank, and means of blanks from three sites during the 2009 spring sampling. It appears that there is little or no difference between the field-trip extended-air blank and the field-trip blank even though the field-trip extended-air blank was exposed 10 times longer than the field-trip blank (20 minutes verses 2 minutes). A paired-sample t-test was done for the two paired results (Yakima and Queets Rivers). This test indicated no difference between results for the field-trip and extended-air blanks (alpha=0.05, P=0.67).



*normalized to 5 SPMD membranes. **dialysis blank with no spike.

Figure 25. Total PBDE in Various Blanks at Three Sites from 2009 Spring Sampling.
Mean: n=3 spring 2009 field-trip blanks; n=2 spring 2009 field-trip extended-air blanks.

PBDE Congeners Found in Blanks

PBDE-47, -99, -100, -153, -154, -183, and -209 were detected in 2007, 2008 and 2009 blanks with a few exceptions. Several PBDE congeners 100 and above were detected below the reporting limits and qualified as estimates. PBDE-100 was detected just above the reporting limits in four blank samples. PBDE-47 and -99 were detected above reporting limits in all blank samples.

PBDE-47 was the largest contributor to total concentration across all samples. PBDE-99 was the second largest contributor.

Figure 26 displays the average percent contribution of detected congeners to the total PBDE sum for 2007, 2008, and 2009 field-trip, field-trip extended-air, and Day0-dialysis blanks.

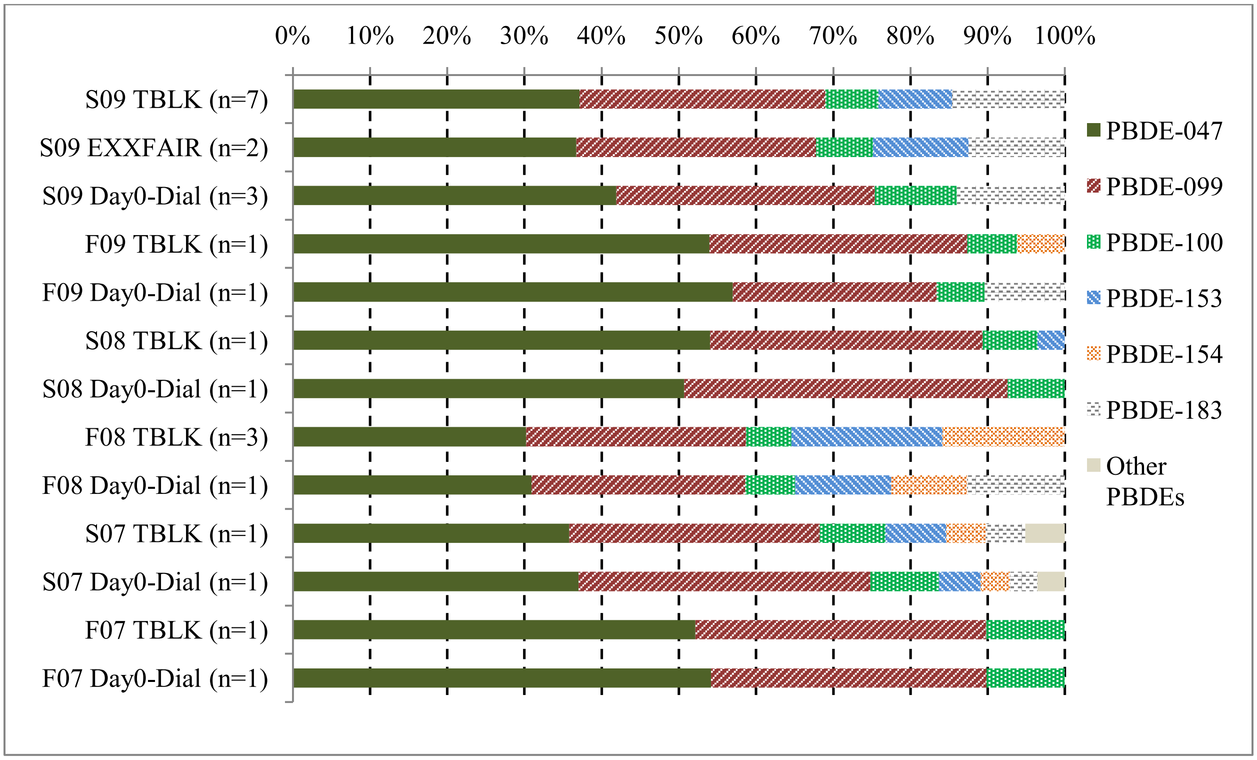


Figure 26. Mean Percent Contribution of Detected PBDE Congeners to Total PBDE Sums Measured in SPMDs Quality Control Blanks for 2007, 2008, and 2009.

S=spring, F=fall, 09=2009, 08=2008, 07=2007, TBLK=field-trip blanks, EXXFAIR = field-trip extended-air blanks, Day0-Dial = Day0-dialysis blanks.

PBDE-47 and -99 contributed 34% - 100% of the total PBDEs in all QC samples for 2007, 2008, and 2009 including QC blanks not shown in the above figure such as the FreshDay0 and Dialysis No Spike blanks. The field samples follow a similar pattern. This is consistent with other studies that have shown the distribution of commercial PBDEs and their breakdown products (Ecology and WDOH, 2006; Sandvik, 2010b; Johnson et al., 2006; and Hale et al., 2003).

Other Observations

The FreshDay0 blanks consisted of only one membrane while other blanks were a composite of five membranes. To make results comparable, the result for the FreshDay0 blank was normalized to five membranes by multiplying the concentration from the single membrane by 5. Normalizing a single membrane result to a multiple membrane result appears to introduce bias which can confound comparisons of results from samples using different numbers of membranes. The ideal solution to this would be to keep the number of membranes consistent across all samples.

PCBs

Overview

Figure 27 shows total PCB results for the 2009 spring sampling. Similar to PBDEs, contamination of the sampling system accounts for a large proportion of the sample result at each site. The results for the seven field-trip blanks range from 26-36 ng/sample and appear to be less variable than results for PBDEs. Again, it is not clear whether the variability among the PCB blanks is due to differences among the air at each site, or is just part of the variability in the SPMDs.

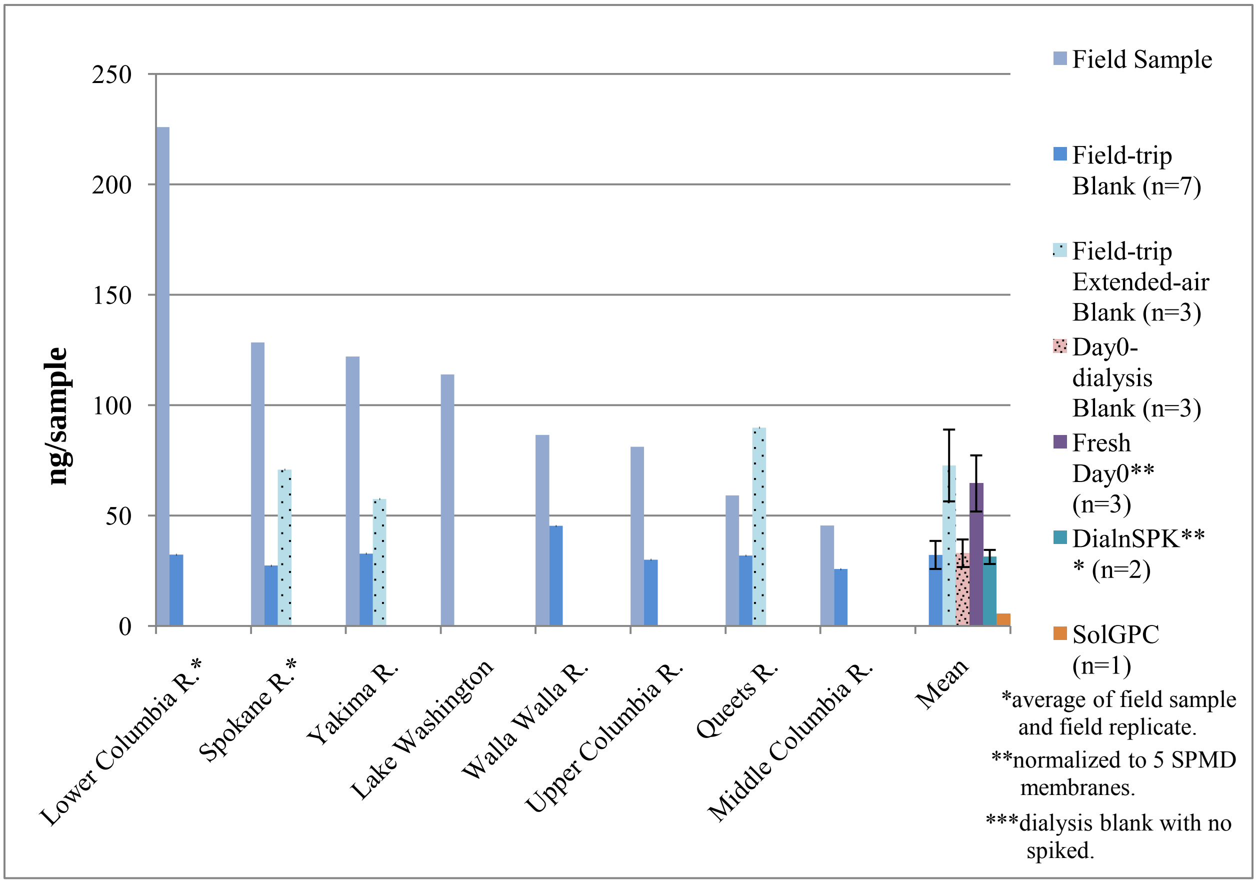


Figure 27. Total PCBs in Sample Results and Blanks from 2009 Spring Sampling.

The "noise" in the sampling system for total PCBs, as represented by field-trip blanks, seems to be around 20-40 ng/sample. This level of noise needs to be considered when using sample results for identifying trends or determining the level of PCBs in a waterbody.

Levels of Contamination in Different Blanks

Figure 28 shows boxplots for PCBs from the 2009 spring blanks and the 2008 fall field-trip blanks. The field-trip, Day0-dialysis, and Dialysis No Spike blanks had similar levels of total PCB. Contamination from air during SPMD deployment and retrieval appears to be minimal when comparing the field-trip and Day0-dialysis blanks. The boxplot for the extended-air blanks show that SPMDs appear to take up some PCBs from the atmosphere over the extended period of 20 minutes. In the 2008 fall sampling, three field-trip blanks were done. These plot slightly higher than the field-trip blanks from the 2009 spring sampling event, thus illustrating some variability from year to year.

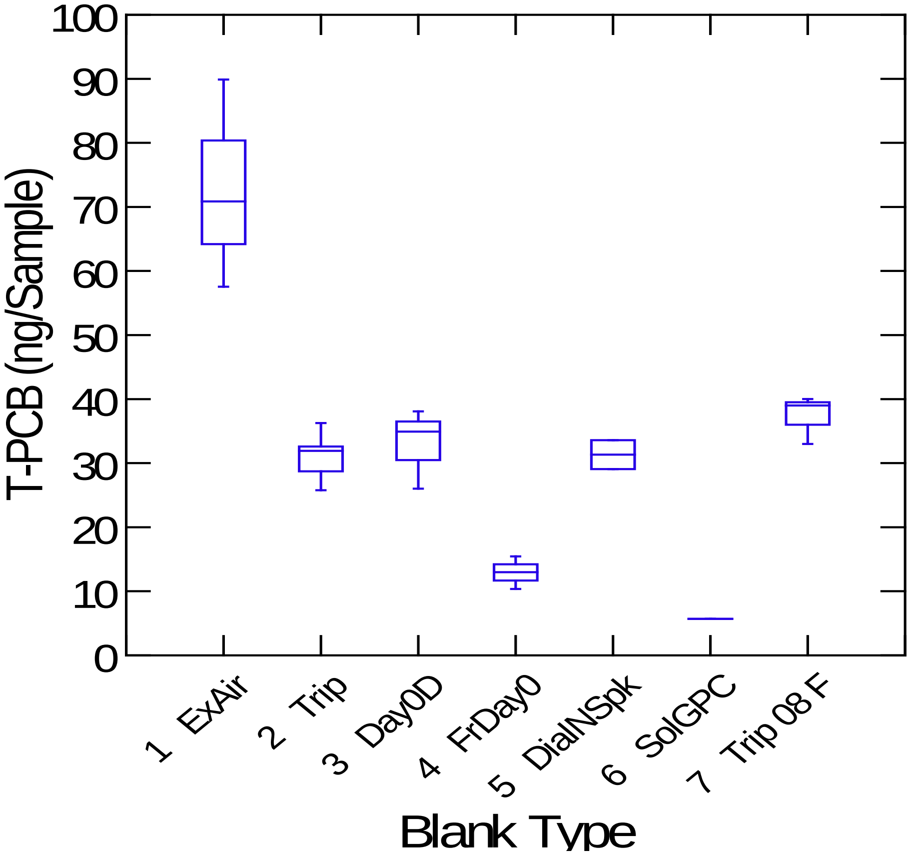


Figure 28. Boxplots Showing Total PCB Results from Various 2009 Spring and 2008 Fall Blanks (ng/sample).

ExAir = field-trip extended-air blanks (n=3), Trip=field-trip blanks (n=7),
Day0-Dial = Day0-dialysis blanks (n=3), FrDay0 = FreshDay0 blanks (n=3),
DialNSpk = dialysis No Spike (n=2), Solvent-GPC blank (n=1), and 2008 fall field-trip blanks (n=3).

Field-trip Blank verses Day0-dialysis Blank

In the fall of 2008, changes in laboratories and other corrective actions were made which appear to have reduced the level of PCB contamination in the field-trip and Day0-dialysis blanks (Figure 29). Total PCBs in the field-trip and Day0-dialysis blanks prior to these changes ranged from about 80-140 ng/sample. The range of contamination now seen in these blanks is about 25-40 ng/sample.

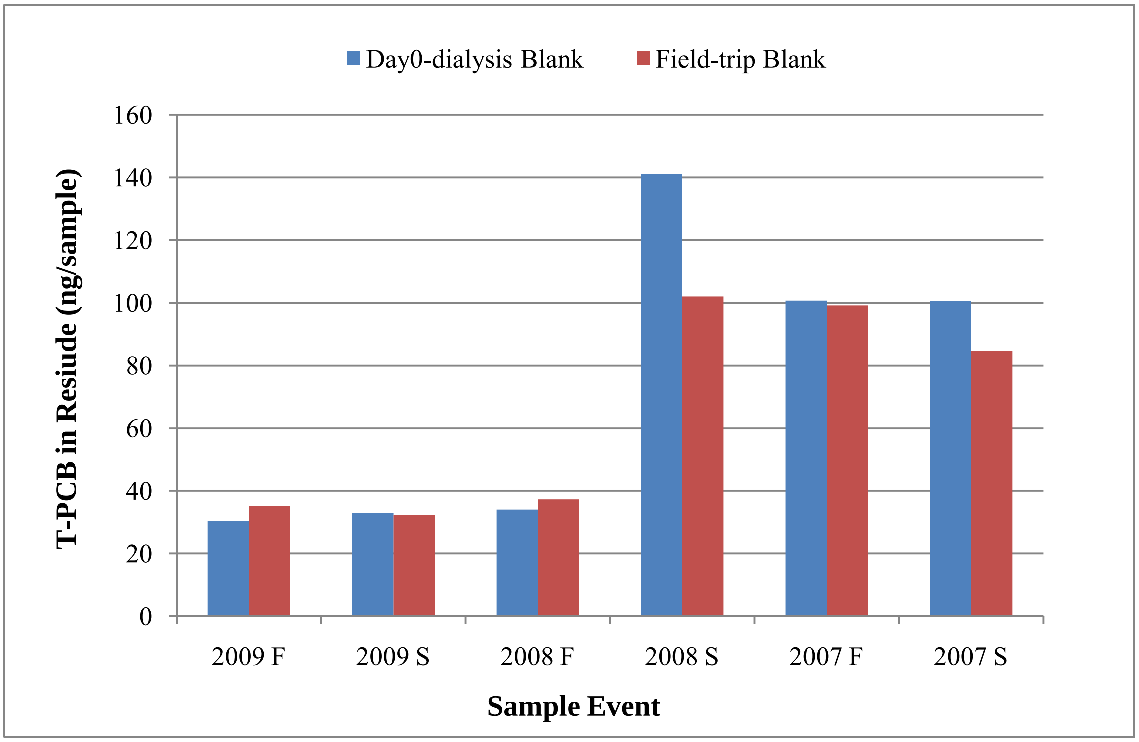


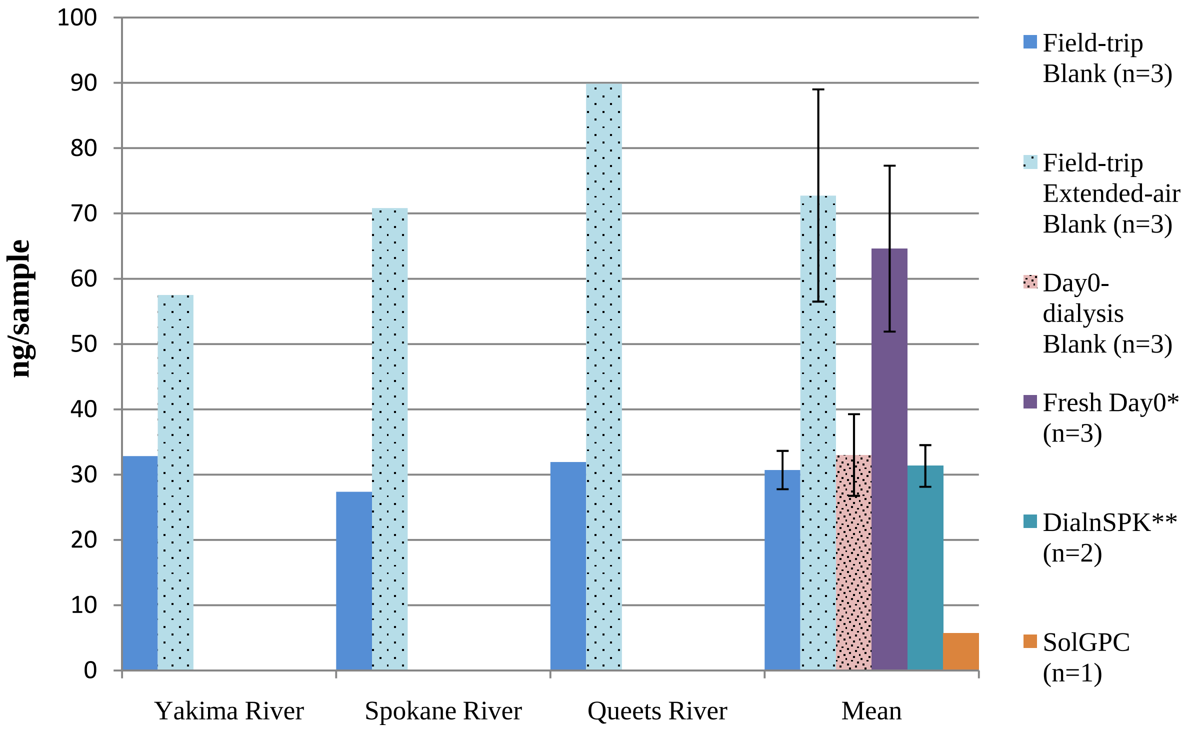
Figure 29. PCBs in the Field-trip and Day0-dialysis Blanks, 2007 – 2009.
S = spring, F = fall.

The observation was shown previously from the boxplots in Figure 28 that contamination from air during SPMD deployment and retrieval is minimal or non-existent. However, if there is contamination from the air, it may be masked by the variability in the results for the blank samples. A paired-sample t-test was performed on the six paired results from the project's beginning in 2007. This test indicated no difference between results for field-trip and Day0-dialysis blanks (alpha=0.05, P=0.29).

Similarly to PBDEs, it may be that the use of both field-trip blanks and Day0-dialysis blanks is not necessary for PCBs. Yet other factors need to be considered before deciding to discontinue one of these blanks, such as: other target analytes from the sample, how the blank is actually exposed (current practice does not mimic the way samples are exposed), and concerns about high variability.

Field-trip Extended-air verses Field-trip Blank

Figure 30 compares results for total PCBs among the field-trip blank, field-trip extended-air blank, and means of blanks from three sites during the 2009 spring sampling. There is a strong indication that SPMDs gain PCBs from ambient air over a 20-minute period. For total PCBs, concentrations in the field-trip extended-air blank ranged from 58-90 ng/sample which is higher than the 28-32 ng/ sample range for the field-trip blank. A paired-sample t-test was done for results from the Yakima, Spokane, and Queets Rivers. This test indicated a difference between results for the field-trip and field-trip extended-air blanks as the boxplots in Figure 28 suggested (alpha=0.05, P=0.05).



*normalized to 5 SPMD membranes. **dialysis blank with no spike.

Figure 30. Total PCBs Compared Among Blanks at Three Sites from 2009 Spring Sampling.
Mean: n=3 spring 2009 field-trip blanks: n=2 spring 2009 field-trip extended-air blanks.

The Queets River site had the highest concentrations in the field-trip extended-air blanks. This site is located in a national forest on the west side of the Olympic Mountains and would seem to be the least affected by anthropogenic activities. It could be that differences among sampling locations (such as air temperature) contributed to the varied levels of contamination in the field-trip extended-air blanks. Or it could be that variability is part of the “noise” in the sampling system. Also, the possibility of atmospheric deposition influence cannot be ruled out. Although monitoring for atmospheric deposition of PCBs may help identify PCB air contaminant sources, it is outside of the scope of this study.

PCB Congeners Found in Blanks

A review of the 2007, 2008, and 2009 data found 20% of PCB congeners (34 of 209 congeners) accounted for about 70% of the contamination in blanks (Table 13).

Table 13. PCB Congeners that Consistently Account for 70% of Contamination in Blanks.

PCB	Range (ng/sample)	Year Detected
Congeners prevalent among blanks		
001	0.129 - 7.19	2007, 2008, & 2009
008	0.309 - 3.94	2007, 2008, & 2009
011	0.181 - 7.13	2007, 2008, & 2009
015	0.113 - 1.6	2007, 2008, & 2009
016	0.157 - 2.4	2007, 2008, & 2009
017	0.196 - 2.57	2007, 2008, & 2009
018/030	0.38 - 5.15	2007, 2008, & 2009
020/028	0.462 - 7.43	2007, 2008, & 2009
021/033	0.254 - 4.38	2007, 2008, & 2009
022	0.129 - 2.31	2007, 2008, & 2009
031	0.44 - 7.62	2007, 2008, & 2009
032	0.125 - 1.68	2007, 2008, & 2009
040/071	0.101 - 2.35	2007, 2008, & 2009
044/047/065	0.276 - 4.83	2007, 2008, & 2009
049/069	0.181 - 2.9	2007, 2008, & 2009
052	0.307 - 5.42	2007, 2008, & 2009
061/070/074/076	0.195 - 11.3	2007, 2008, & 2009
064	0.0896 - 2.23	2007, 2008, & 2009
066	0.0846 - 5.63	2007, 2008, & 2009
090/101/113	0.0981 - 3.16	2007, 2008, & 2009
095	0.123 - 2.57	2007, 2008, & 2009
147/149	0.067 - 1.36	2007, 2008, & 2009
Other congeners found in blanks		
004	0.113 - 0.639	2008 & 2009
010	5.48	2007
025	0.209 - 19.3	2007
026/029	0.104 - 0.609	2008 & 2009
050/053	0.0904 - 0.511	2008
056	0.071 - 2.89	2008
086/087/097/108/119/125	0.0392 - 2.68	2008 & 2009
099	0.86 - 2.51	2008
110	0.0453 - 3.82	2007 & 2008
118	0.262 - 2.8	2008
141	1.38 - 1.8	2007
184	0.846 - 2.39	2008

A total of 22 individual congeners and co-eluting groups (about 13%) were prevalent among all blanks and contributed about 70% contamination in all three sampling years to date. This agrees with earlier findings when reviewing the 2008 samples (Sandvik and Seiders, 2009). Of the 12 additional congeners listed in Table 13 at the 70% evaluation level, nine were found to be prevalent among blanks when evaluated for 80% contamination, which support the congeners be considered among the background contaminants. Of the remaining three congeners, two could also be considered among background contaminants as they were at or above the 80% evaluation level, just not quite as prevalent: PCB-141 was found in 2007 blanks (four samples), and PCB-184 was found in 2008 spring blanks (two samples).

Only PCB-010 was found to be a possible anomaly for a background contaminant from this list. PCB-010 was found in a single Day0-dialysis from the fall of 2007 at high concentrations (upper 35% contributor level). Certain laboratory and spiking solution contaminations were found in the 2007 results (Sandvik, 2008) making it difficult to decipher background verses laboratory contamination and at what level. The high levels and isolated detection event suggest PCB-010 may be a product of the 2007 contamination issues rather than part of a background group of congeners.

The largest PCB contributor to total concentration varied somewhat among the blank samples. PCB-031 was the largest contributor to total concentration followed by PCB-020/028 contributing over 7 % each on average across all blank samples. Figure 31 displays the average percent contribution of the 22 congeners and co-eluting groups that contribute 70% to the total PCB sum for 2007, 2008, and 2009 field-trip, field-trip extended-air, and Day0-dialysis blanks.

PCB-031 and -052 plus co-elute groups of PCB-018/030, -020/028, -021/033, and -061/070/074/076 contributed 19% - 31% of the total PCBs in all QC samples for 2007, 2008, and 2009 blanks including QC blanks not shown in the above figure such as the FreshDay0 and Dialysis No Spiked blanks. The field samples follow a similar pattern with the exception that several field samples show levels of PCB-011 contributing greater than 20% to total PCBs. Recent studies are reporting PCB-011 to be a global pollutant from inadvertent production of pigments or dyes (Dingfei and Hornbuckle, 2010; Muñoz, 2007; Rodenburg et al., 2010).

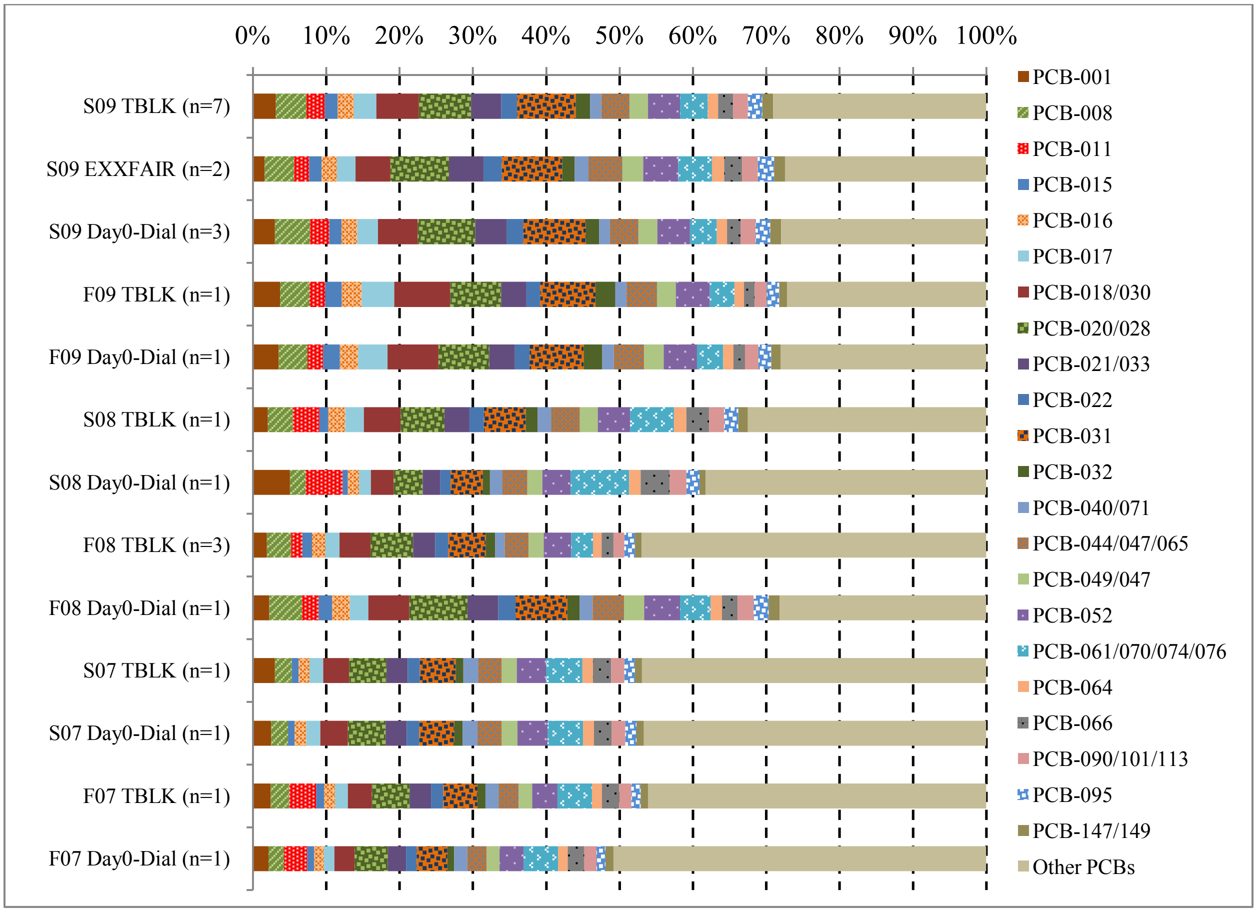


Figure 31. Mean Percent Contribution of Major (70%) PCB Congeners and Co-eluting groups to Total PCB Sums Measured in SPMDs Quality Control Blanks for 2007, 2008, and 2009.

S=spring, F=fall, 09=2009, 08=2008, 07=2007, TBLK=field-trip blanks, EXXFAIR = field-trip extended-air blanks, Day0-Dial = Day0-dialysis blanks.

PAHs

Overview

Figure 32 shows total PAH results for the 2009 spring sampling. It is clear that levels of contamination account for a large proportion of the sample result at each site. Another observation is that the results for the seven field-trip blanks are quite variable. As with PBDEs and PCBs, the source of this variability is not clear: it could be due to differences at each site or part of the variability in the SPMDs themselves. The "noise" in the sampling system for total PAH (as represented by field-trip blanks) seems to be in the range of 300-500 ng/sample.

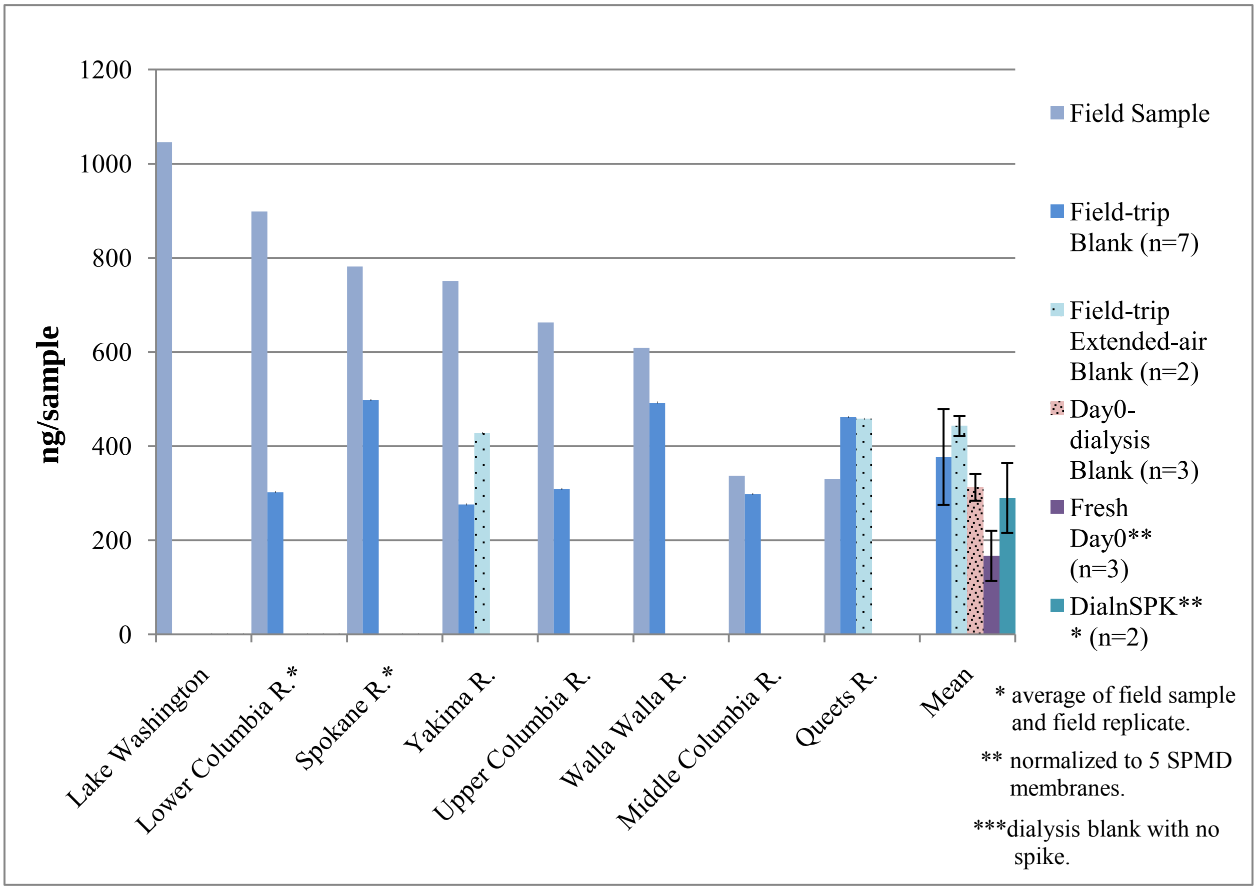


Figure 32. Total PAHs in Sample Results and Blanks from 2009 Spring Sampling.

Levels of Contamination in Different Blanks

Figure 33 shows the range of values for total PAH (T-PAH) from the 2009 spring blanks and 2008 fall field-trip blanks. The field-trip blanks show a large range, while the Day0-dialysis and field-trip extended-air blanks show much smaller ranges.

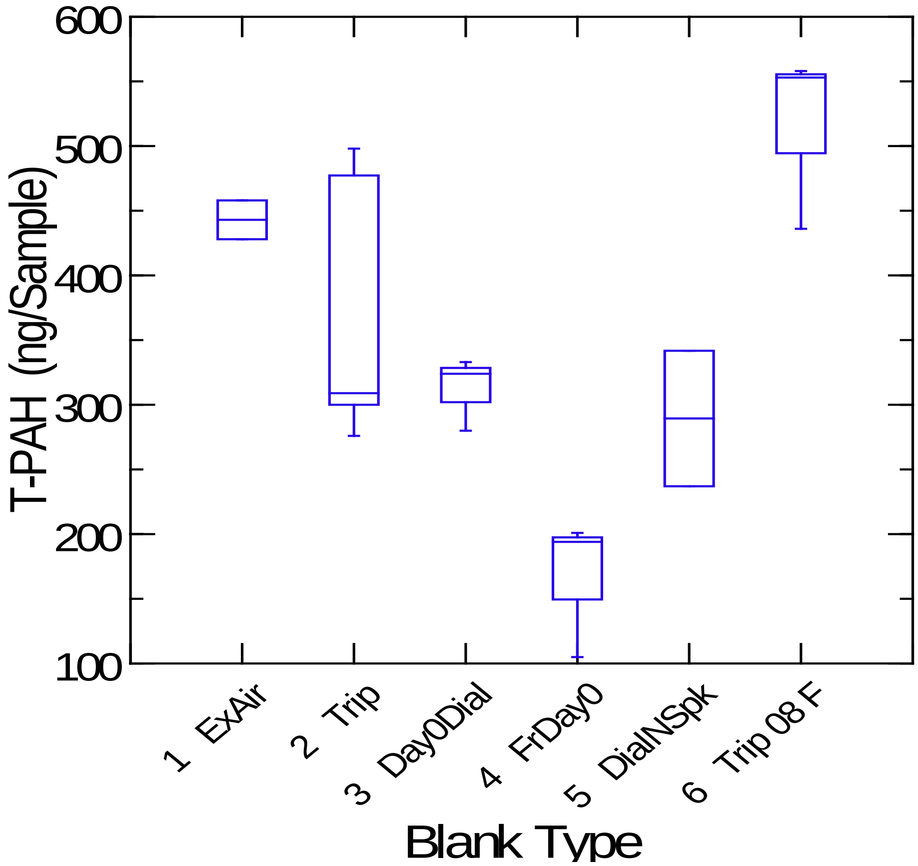


Figure 33. Boxplots Showing Total PAH Results from Various 2009 Spring and 2008 Fall Blanks (ng/sample).

ExAir = field-trip extended-air blanks (n=2), Trip=field-trip blanks (n=7),
Day0-Dial = Day0-dialysis blanks (n=3), FrDay0 = FreshDay0 blanks (n=3),
DialNSpk = dialysis blank with no spikes (n=2), 2008 Fall Trip blank (n=3).

Field-trip Blank verses Day0-dialysis Blank

Figure 34 shows field-trip and Day0-dialysis results for T-PAH, LPAH, and HPAH from four sampling events during 2008 and 2009. LPAH is a larger source of contamination than is HPAH. Levels of contamination for all groups appear to vary over time with no consistent pattern. A paired-sample t-test using the six paired results from the project's beginning in 2007 indicated no difference between results for field-trip and Day0-dialysis blanks (alpha=0.05, P=0.75).

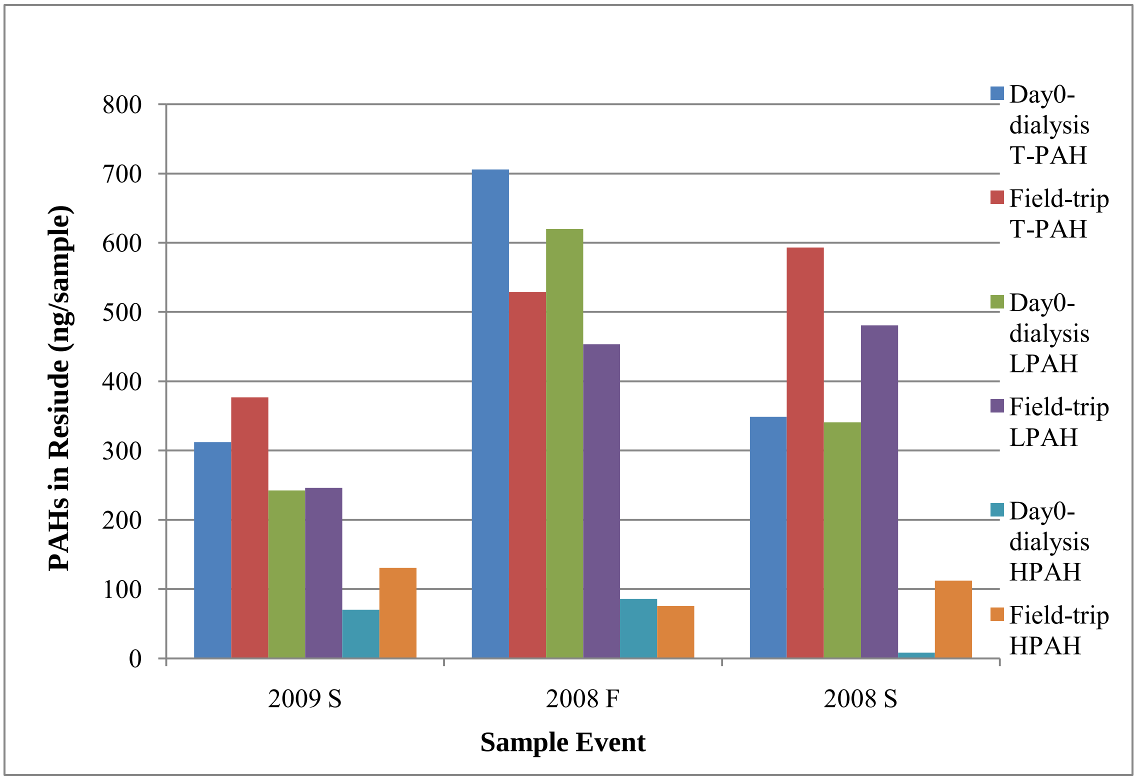


Figure 34. PAHs in the Field-trip and Day0-dialysis Blanks, 2008 and 2009.
S = spring, F = fall.

It may be that for PAHs, the use of both field-trip blanks and Day0-dialysis blanks is not necessary. Yet other factors need to be considered before deciding to discontinue one of these blanks, such as: other target analytes from the sample, how the blank is actually exposed (current practice does not mimic the way samples are exposed), and concerns about high variability.

Field-trip Extended-air verses Field-trip Blank

Figure 35 compares results for total PAH among the field-trip blank, field-trip extended-air blank, and means of blanks from three sites for total PAH during the 2009 spring sampling. Like PBDEs and PCBs, levels of contamination in blanks from exposure to air varied among samples with no clear pattern. A paired-sample t-test was done for field-trip and Day0-dialysis results from the Yakima and Queets Rivers. This test indicated no difference between results for the field-trip and field-trip extended-air blanks (alpha=0.05, P=0.52).

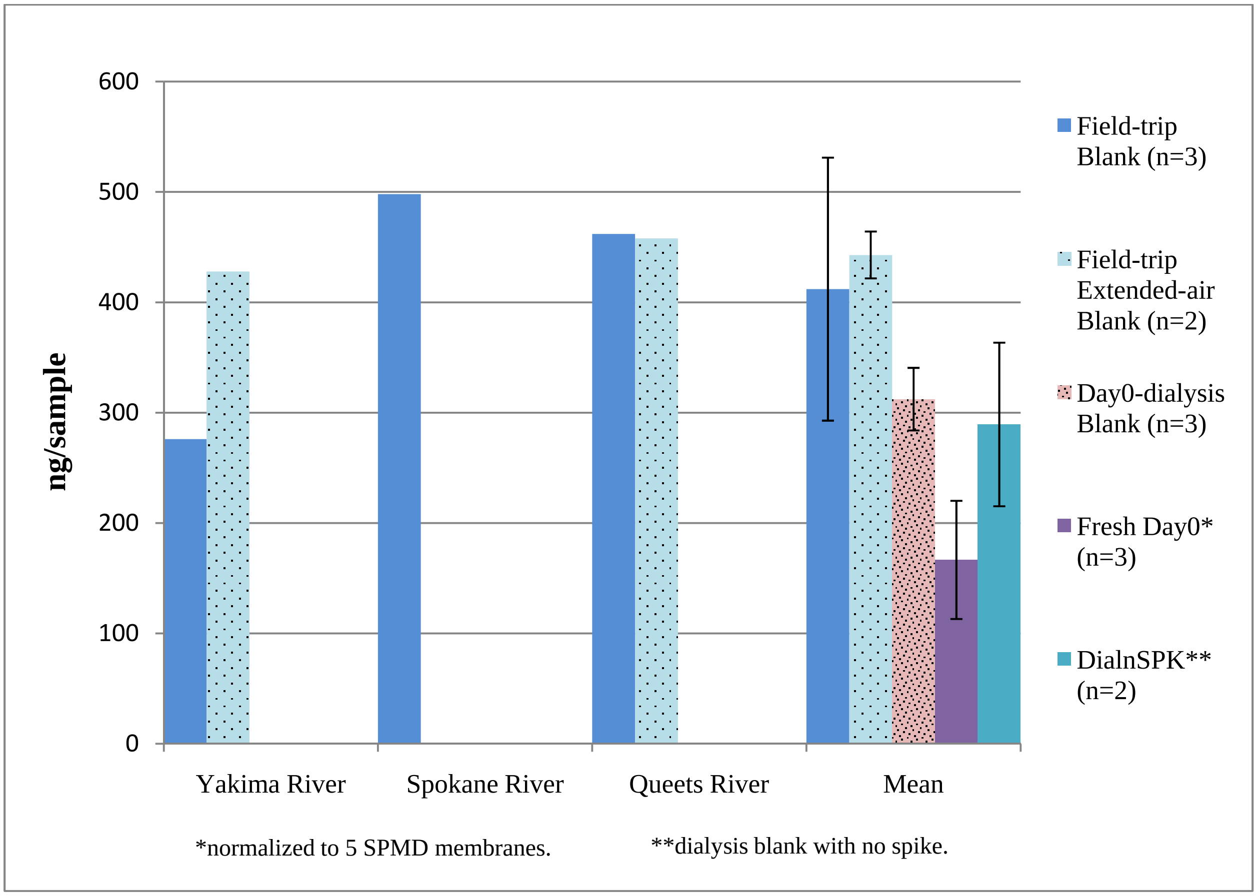


Figure 35. Total PAHs Compared Among Blanks at Three Sites from 2009 Spring Sampling.
Mean: n=3 spring 2009 field-trip blanks; n=2 spring 2009 field-trip extended-air blanks.

PAHs Found in Blanks

PAH blank contaminants were limited to six analytes commonly found in the field-trip blanks and also in all the other QC blanks. This same pattern was seen in the 2008 PBT Trends Study. There were no PAHs sampled in 2007. Another six analytes were detected among various blanks. Table 14 list the PAH blank contaminants for 2008 and 2009.

Table 14. 2008 and 2009 PAH Blank Detections.

Parameter	Range (ng/sample)	Year Detected
1-Methylnaphthalene	89 - 400	2008 & 2009
2-Methylnaphthalene	180 - 430	2008 & 2009
Naphthalene	100 - 290	2008 & 2009
Phenanthrene	55 - 240	2008 & 2009
Dibenzofuran	45 - 120	2008 & 2009
Fluorene	40 - 170	2008
Fluoranthene	62 - 90	2008 & 2009
Benzo(a)anthracene	66 - 68	2009
Benzo(b)fluoranthene	46 - 51	2009
Benzo(k)fluoranthene	46 - 50	2009
Retene	70 - 83	2008
Pyrene	40 - 44	2008

Blank Correction

Contamination of the measurement system has been a concern in many Ecology projects using SPMDs because the level of contamination is high relative to what has been measured in the environment. The variability of this contamination is also a concern because the variability can affect the quality of results depending on how blank-correction is performed. The practice of blank-correction is controversial, and there are no easy solutions to this issue.

Various methods for blank-correction have been used across Ecology studies. The different methods yield different results, which compromises the usefulness and comparability of results. No standard procedure for blank correction has been promoted, and the methods suggested by developers of the SPMD system can lead to negative results. Ecology SPMD projects have typically used a single field-trip blank to characterize contamination encountered in the field during deployment and retrieval of SPMDs. The implied and untested assumption has been that a single blank at any one site adequately represents the level of contamination from air during deployment and retrieval at all sites.

Blank correction methods used in previous Ecology studies include:

1. Sample Result (SR) minus Field Blank (FB) = Corrected Sample Result (CSR).
   This can and has led to negative results.

2. SR minus FB = CSR, only if SR > 3x FB.
   If SR < 3x FB, no correction done, SR reported as is and flagged.

3. If FB contaminated, then SR minus FB = CSR.
   If FB not contaminated, then SR minus DayZero/Dialysis Blank = CSR.

4. SR minus the mean of multiple FBs = CSR.

5. SR rejected if FB is high relative to SR, or SR not reported: “high” not defined.

6. SR minus the mean of multiple FBs = CSR; only if SR > mean + 2 standard deviations of the FB (method used in this 2009 report).

The approach in #6 above is similar to that used in the EPA 1600 method series. In these methods, EPA requires that a minimum of ten blanks be used before blank-correcting data. The large number of blanks is needed to adequately characterize the variability, or noise, in the measurement system. The use of ten blanks is cost-prohibitive for many sampling efforts with SPMDs, requiring a choice between the quality of data versus the quantity of data.

To help balance the quality and quantity of results, it is recommended that each project carefully consider and document how it plans to address background contamination. A one-size-fits-all approach is unrealistic because of the varied goals that projects may have. For example, screening level studies may not need as much quantitative rigor as trend monitoring studies or studies that might result in regulatory actions.

For trend monitoring and support of regulatory actions, multiple blanks as in approach #6 above should be used. For screening-level studies, approach #2 above may be adequate in the absence of multiple blanks and is more appropriate than the other approaches. Based the ratios of standard deviations to means from using multiple blanks, approach #2 should yield acceptable estimates of contaminants in ambient waters, such as natural waters where the levels of contamination by PBDEs, PCBs, or PAHs are relatively low.

For waters that may have higher levels of these and other contaminants, such as wastewater effluent or stormwater, the noise in the measurement system (background contamination) may be so low as to not require blank-correction. Each SPMD project should consider and document how it plans to address background contamination.

Another concern with blank-corrected results is that the level of confidence in the results is difficult to estimate, especially when using less than the ten blanks as recommended in the EPA 1600 method series. Determining a level of confidence when fewer blanks are used in correction would involve statistical evaluations that are beyond the resources typically given SPMD monitoring efforts. However, such evaluations should be pursued to gain greater certainty about the quality of data produced by SPMDs.

Conclusions

Major findings from efforts to better characterize data quality in this 2009 PBT Trends Study are:

- Previous QC efforts identified major sources of PCB contamination in the measurement system (solvents and laboratory), and corrective actions reduced the level of contamination. This also occurred with certain CPs. There were no CPs detected in any blanks in 2009, but many analytes were found in the other chemical groups (PAHs, PBDEs, and PCBs).

- QC efforts conducted during the 2009 spring sampling improved characterization of the sources and relative magnitudes of contamination for PBDEs, PCBs, and PAHs:
    - Fabrication, storage, dialysis, and GPC processes for SPMDs account for 60% - 90% of contamination.
    - The spiking processes account for 10% - 30% of contamination.
    - Exposure to air during deployment and retrieval of SPMDs accounts for about 0% - 15% of contamination.
    - Contamination from the analytical laboratories currently used seems inconsequential.

- The level of "background" contamination varied among analytes during the 2009 spring sampling: total PBDEs, 30-55 ng/sample; total PCBs, 25-35 ng/sample; and total PAH, 300-500 ng/sample.

- The background level of contamination also varies among sampling events, as shown by the comparison to the 2008 fall samples: total PBDEs, 50-75 ng/sample; total PCBs, 35-40 ng/sample; and total PAH, 430-570 ng/sample.

- Further reduction of contamination from PBDEs, PCBs, and PAHs seems unlikely without larger investigative efforts which would need to include operations where SPMDs are fabricated and processed prior to lab analysis.

- The "noise" in the SPMD measurement system accounts for a significant part of the contaminant levels detected in environmental samples at many sites, especially sites with lower levels of contaminants.

- The variability of contaminant levels throughout the SPMD measurement system is high enough that the variability must be considered when using blank-correction to adjust results.

- The ability to measure spatial or temporal trends with SPMDs at many sites is compromised because contaminant levels at some sites are low relative to the noise in the sampling system. The level of certainty associated with blank-corrected results for use in trend analyses is unclear and will likely reduce the sensitivity of any analyses for trends.

- The field-trip blank, as currently handled, may under-represent contamination from the environment as the field-trip blank is intended to do.

- There appears to be no difference between results from the field-trip and Day0-dialysis blanks, which suggests that contamination from air exposure during deployment and retrieval is negligible.

- There is strong indication of a difference between results from the field-trip and field-trip extended-air blanks for PCBs, but not for the other analytes. This suggests that PCBs may be gained from ambient air in long-term air exposure. Background noise, differences among sampling locations, or atmospheric deposition may play a part in elevated concentrations.

- Specific analyte contamination found in blanks is summarized below:
    - PAH blank contaminants were limited to six analytes. The overall environmental risk was determined to be low from the low levels of PAH found in the field samples.
    - PBDE-47, -99, -100, -153, -183, and -209 were detected in blanks. Several PBDE congeners (PBDE-100, -153, -183, and -209) were detected below the reporting limit and qualified as estimates. PBDE-47 and -99 were detected above the reporting limit in all blank samples and were the major contributors to total PBDEs.
    - A total of 20% (or 34 congeners) of PCB analytes accounted for about 70% of the contamination in QC blanks. 22 individual congeners and co-eluting groups (about 13%) were prevalent among all blanks in all the sampling years to date.
    - Elevated levels of PCB-011 (>20% contribution to total PCBs) were found in several field samples but not consistently in all field samples, indicating an outside source rather than a background contaminant at this level.

Recommendations

Recommendations from efforts to better characterize data quality in this 2009 PBT Trends Study include:

- Continue analyzing the following blanks until additional reviews of data quality concerns and model needs are completed. Specifically:
    - Use a field-trip blank at each site that is monitored in order to better characterize the level and variability of contamination from SPMD field deployment and retrieval. This is the procedure recommended by the developers of the SPMD system.
    - Include the Day0-dialysis blank for each SPMD sampling period to define the variability of contaminant (particularly PCB and PBDE) background levels during SPMD manufacturing.
    - Review other blank data (historical and current) to help reach a final decision on the usefulness of these blanks.
    - Drop the use of FreshDay0 blank because it appears to provide little value.
- Investigate the adequacy of the field-trip blank at representing sources of contamination. This would involve side-by-side comparisons of different handling procedures of the field-trip blank.
- Ensure that laboratories performing analyses demonstrate that their reagents and processes are free of contaminants at levels specified in work plans and contracts.
- Enlist the services of staff at Ecology's Laboratory Accreditation Unit and MEL to evaluate the uncertainty of, and quality of, results obtained from blank-correcting SPMD data.

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APPENDICES

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Appendix A. Chemicals from Ecology's PBT Initiative

Table A-1. Persistent Bioaccumulative Toxic (PBT) Chemical List.

Metals	Flame Retardants	Banned Pesticides	Organic Chemicals
Methyl-Mercury	PBDEs Tetrabromobisphenol A Hexabromocyclododecane Pentachlorobenzene	Aldrin/Dieldrin Chlordane DDT/DDD/DDE Heptachlor Epoxide Toxaphene Chlordecone Endrin Mirex	1,2,4,5-TCB Perfluoro-octane Sulfonates Hexachlorobenzene Hexachlorobutadiene Short-chain chlor paraffins Polychlorinated Naphthalenes

Combustion By-Products	Banned Flame Retardants	Banned Organic Chemicals	Metals of Concern
PAHs PCDDs PCDFs PBDD/PBDF	Hexabromobiphenyl	PCBs	Cadmium Lead

Appendix B. Monitoring Site Descriptions

Table B-1. Sample Site Descriptions, 2009 PBT Trends Study.

Site Name	County	Sampling Dates		Site Description	Latitude[1]	Longitude[1]	WBID [2]	WRIA Number	EIM "User Location ID" [3]
		Deployed	Retrieved		Decimal Degrees				
Lower Columbia R.	Wahkiakum	4/29/09	5/27/09	Columbia River, RM 54.	46.1849	-123.1876	WA-CR-1010	25	SPMDTR-LCR2
Lower Columbia R. Replicate	Wahkiakum	4/29/09	5/27/09	Columbia River, RM 54.	46.1849	-123.1876	WA-CR-1010	25	SPMDTR-REPLCR
Mid Columbia R.	Benton	4/30/09	5/28/09	Columbia River, McNary Dam, RM 292.0.	45.9394	-119.2972	WA-CR-1026	31	SPMDTR-MCR
Queets R.	Jefferson	5/4/09	6/1/09	Queets River, RM 11.5.	47.5522	-124.1978	WA-21-1030	21	SPMDTR-QUEETS
Spokane R.	Spokane	4/30/09 9/3/09	5/28/09 9/30/09	Spokane River, Nine Mile Dam, RM 58.1.	47.7747	-117.5444	WA-54-1020	54	SPMDTR-SPOK
Spokane R. Replicate	Spokane	4/30/09 9/3/09	5/28/09 9/30/09	Spokane River, Nine Mile Dam, RM 58.1.	47.7747	-117.5444	WA-54-1020	54	SPMDTR-REPSPOK
Spokane R.	Spokane	9/3/09	9/30/09	Spokane River, near Idaho border, RM 98.3.	47.6942	-117.0094	WA-57-1010	57	SPMDTR-SPOKBD
Upper Columbia R.	Chelan-Douglas	4/28/09	5/26/09	Columbia River, Rock Island Dam, RM 453.5.	47.3439	-120.0939	WA-CR-1040	44	SPMDTR-UCR
Walla Walla R.	Walla Walla	4/30/09	5/28/09	Walla Walla River, RM 9.	46.0709	-118.8268	WA-32-1010	32	SPMDTR-WALLA
Washington L.	King	4/28/09	5/26/09	Lake Washington, outlet.	47.6475	-122.3019	WA-08-9350	8	SPMDTR-LKWA2
Yakima R.	Benton	4/30/09	5/28/09	Yakima River, Wanawish Dam, RM 18.0.	46.3783	-119.4181	WA-37-1010	37	SPMDTR-YAK
Yakima R. Replicate	Benton	4/30/09	5/28/09	Yakima River, Wanawish Dam, RM 18.0.	46.3783	-119.4181	WA-37-1010	37	SPMDTR-REPYAK

1. North American Datum 1983 is horizontal datum for coordinates.
2. Ecology's Water Body Identification Number (WBID).
3. Site identification as used in Ecology's Environmental Information Management (EIM) system.

Appendix C. Chemicals Analyzed in SPMD Samples

Table C-1. Chemicals Analyzed in SPMD Samples Collected During 2009.

Chlorinated Pesticides (MEL PEST2)
alpha-BHC
beta-BHC
gamma-BHC (lindane)
delta-BHC
Heptachlor
Aldrin*
Chlorpyriphos
Heptachlor epoxide*
trans-chlordane (gamma)*

cis-chlordane (alpha)*
Endosulfan I (Alpha-endosulfan)
Dieldrin*
Endrin*
Endrin Ketone
Endosulfan II (Beta-endosulfan)
Endrin Aldehyde
Endosulfan Sulfate
4,4'-DDE*
4,4'-DDD*
4,4'-DDT*
2,4-DDE
2,4'-DDD
2,4'-DDT
Methoxychlor
Oxychlordane
DDMU
Cis-nonachlor
Toxaphene*
Trans-nonachlor
Mirex*
Chlordane (technical)*
Hexachlorobenzene*
Dacthal (DCPA)
Pentachloroanisole

Polychlorinated Biphenyls*[1]

Polybrominated Diphenyl Ethers*
PBDE-47
PBDE-49
PBDE-66
PBDE-71
PBDE-99
PBDE-100
PBDE-138
PBDE-153
PBDE-154
PBDE-183
PBDE-184
PBDE-191
PBDE-209

*PBTs as defined by Ecology.

[1] Approximately 170 individual PCB congeners and the remainders as co-eluting groups.

Table C-1. (continued)

Polycyclic Aromatic Hydrocarbons*

Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
2-Chloronaphthalene
Acenaphthylene
Acenaphthene
Dibenzofuran
Fluorene
Phenanthrene
Anthracene
Carbazole
Fluoranthene
Pyrene
Retene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenzo(a,h)anthracene
Benzo(ghi)perylene

Appendix D. Mean Water Temperature and Exposure Times

Table D-1. Mean Water Temperature and Water Exposure Times for SPMD Samples, 2009.

Site	April-May		Aug.-Sept.	
	Temp (ºC)	Time (days)	Temp (ºC)	Time (days)
Lower Columbia River	11.7	27.9	-	-
Middle Columbia River at McNary Dam	16.7	27.9	-	-
Upper Columbia River at Rock Island Dam	8.6	28.0	-	-
Queets River	9.8	27.9	-	-
Yakima River at Wanawish Dam	15.4	27.9	-	-
Walla Walla River	13.1	27.9	-	-
Spokane River at Nine Mile Dam	10.0	28.0	14.8	27.1
Lake Washington	13.6	27.9	-	-
Lower Columbia River Replicate	12.1	28.0	-	-
Spokane River at Nine Mile Dam Replicate	9.9	28.0	-	-
Yakima River at Wanawish Dam Replicate*	14.0	-	-	-
Spokane River near Idaho Border	-	-	19.5	27.1

- not available. Did not sample. Yakima spring replicate lost.
*Yakima spring replicate temperature recorded but SPMD sample compromised.

Appendix E. Performance Reference Compound (PRC) Recovery in SPMDs

Table E-1. 2009 PRC Sample Recovery (Spring).

PRCs spiked in each membrane. Samples = 5 membranes.

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration[1] (ng/sample)	Recovered (%)
Lower Columbia River	090604301	PCB-004	34.4	17%
		PCB-029	128	64%
		PCB-050	156	78%
Middle Columbia River	090604302	PCB-004	32.5	16%
		PCB-029	87.6	44%
		PCB-050	88.8	44%
Upper Columbia River	090604303	PCB-004	55.6	28%
		PCB-029	151	76%
		PCB-050	150	75%
Queets River	090604304	PCB-004	68.8	34%
		PCB-029	156	78%
		PCB-050	188	94%
Yakima River	090604305	PCB-004	34.7	17%
		PCB-029	131	66%
		PCB-050	139	70%
Walla Walla River	090604306	PCB-004	34.9	17%
		PCB-029	124	62%
		PCB-050	136	68%
Spokane River	090604307	PCB-004	34.4	17%
		PCB-029	128	64%
		PCB-050	159	80%
Lake Washington	090604308	PCB-004	49.2	25%
		PCB-029	126	63%
		PCB-050	130	65%
Lower Columbia River Replicate	090604313	PCB-004	35.1	18%
		PCB-029	119	60%
		PCB-050	153	77%
Spokane River Replicate	090604314	PCB-004	34.1	17%
		PCB-029	135	68%
		PCB-050	166	83%

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration[1] (ng/sample)	Recovered (%)
Field-trip Blank – Lower Columbia R.	090604316	PCB-004	115	58%
		PCB-029	140	70%
		PCB-050	159	80%
Field-trip Blank – Upper Columbia R.	090604317	PCB-004	124	62%
		PCB-029	155	78%
		PCB-050	150	75%
Field-trip Blank – Yakima Columbia R.	090604318	PCB-004	96.8	48%
		PCB-029	138	69%
		PCB-050	135	68%
Field-trip Blank – Middle Columbia R.	090604319	PCB-004	113	57%
		PCB-029	135	68%
		PCB-050	125	63%
Field-trip Blank – Walla Walla R.	090604320	PCB-004	77.4	48%
		PCB-029	112	70%
		PCB-050	108	54%
Field-trip Blank – Spokane R.	090604321	PCB-004	102	51%
		PCB-029	130	65%
		PCB-050	124	62%
Field-trip Blank – Queets R.	090604322	PCB-004	130	65%
		PCB-029	160	80%
		PCB-050	158	79%
Field-trip Extended-air Blank – Yakima R.	090604323	PCB-004	113	57%
		PCB-029	163	82%
		PCB-050	169	85%
Field-trip Extended-air Blank – Spokane R.	090604324	PCB-004	130	65%
		PCB-029	179	90%
		PCB-050	182	91%
Field-trip Extended-air Blank – Lower Columbia R.	090604325	PCB-004	158	79%
		PCB-029	209	105%
		PCB-050	202	101%
Day0-dialysis Blank 1	090604326	PCB-004	122	61%
		PCB-029	173	87%
		PCB-050	163	82%
Day0-dialysis Blank 2	090604327	PCB-004	114	57%
		PCB-029	170	85%
		PCB-050	163	82%

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration[1] (ng/sample)	Recovered (%)
Day0-dialysis Blank 3	090604328	PCB-004	121	61%
		PCB-029	174	87%
		PCB-050	166	83%
FreshDay0-dialysis Blank 1[2]	090604332	PCB-004	9.95	50%
		PCB-029	12.8	64%
		PCB-050	14.4	72%
FreshDay0-dialysis Blank 2[2]	090604333	PCB-004	12.65	63%
		PCB-029	15.55	78%
		PCB-050	17.95	90%
FreshDay0-dialysis Blank 3[2]	090604334	PCB-004	11.8	59%
		PCB-029	14.75	74%
		PCB-050	15.75	79%

[1] Spring initial concentration = 200 ng/sample. [2] Spring initial concentration = 40 ng/sample.

Table E-2. 2009 PRC Sample Recovery (Fall).

PRCs spiked in each membrane. Samples = 5 membranes.

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration[1] (ng/sample)	Recovered (%)
Spokane River at Nine Mile Dam	091002607	PCB-004	53.7	27%
		PCB-029	126	63%
		PCB-050	129	65%
Spokane River near Idaho Border	091002643	PCB-004	34.7	17%
		PCB-029	125	63%
		PCB-050	137	69%
Field-trip Blank – Spokane R. at Nine Mile Dam	091002621	PCB-004	116	58%
		PCB-029	148	74%
		PCB-050	150	75%
Day0-dialysis Blank 1	091002626	PCB-004	101	51%
		PCB-029	136	68%
		PCB-050	139	70%
FreshDay0-dialysis Blank 1[2]	091002632	PCB-004	22.0	55%
		PCB-029	29.2	73%
		PCB-050	30.0	75%

[1] Fall initial concentration = 200 ng/sample. [2] Fall initial concentration = 40 ng/sample.

Appendix F. Log K_{ow}s Used to Estimate Water Concentration.

Table F-1. Log K_{ow}s Used in the USGS Estimated Water Concentration Calculator Spreadsheet for the 2009 PBT Trends Study.

Organochlorine Pesticides	Log K_{ow}	Ref.
p,p'-DDT	5.47	a
p,p'-DDE	6.14	a
p,p'-DDD	5.75	a
o,p'-DDT	5.59	a
o,p'-DDE	5.56	a
o,p'-DDD	6.08	a
DDMU	5.50	e
Dieldrin	4.60	a
Chlorpyrifos	4.90	f
Endosulfan I	3.78	a
Endosulfan-II	3.50	e
Endosulfan Sulfate	3.64	e
Hexachlorobenzene (HCB)	5.71	a
Pentachloroanisole (PCA)	5.48	b, e
Toxaphene	4.73	a
Chlordane (technical)	6.29	e
trans-Chlordane	5.38	a, c, d, e
cis-Chlordane	5.38	a, c, d, e
Dacthal	4.26	e
trans-Nonachlor	6.35	c, e
cis-Nonachlor	6.20	c, e
Heptachlor	5.19	a
Heptachlor Epoxide	4.51	a
alpha-Benzenehexachloride (a-BHC)	3.86	a
beta-Benzenehexachloride (b-BHC)	3.86	a
delta-Benzenehexachloride (d-BHC)	4.12	a
Lindane	3.71	a
Aldrin	5.97	e, i
Endrin	4.63	a
Endrin ketone	4.99	e
Endrin aldehyde	4.80	e
Mirex	6.89	a
p,p'-Methoxychlor	4.61	a
Oxychlordane	5.48	e

PAHs	Log K_{ow}	Ref.
Naphthalene	3.45	k
2-Methylnaphthalene	3.86	l
1-Methylnaphthalene	3.86	l
2-Chloronaphthalene	3.81	e
Acenaphthylene	4.08	k
Acenaphthene	4.22	k
Dibenzofuran	4.12	l
Fluorene	4.38	k
Phenanthrene	4.46	k
Anthracene	4.54	k
Carbazole	3.23	e
Fluoranthene	5.20	k
Pyrene	5.30	k
Retene	6.35	e
Benzo(a)anthracene	5.91	k
Chrysene	5.61	k
Benzo(b)fluoranthene	5.78	k
Benzo(k)fluoranthene	6.20	k
Benzo(a)pyrene	6.35	k
Indeno(1,2,3-cd)pyrene	6.75	k
Dibenzo(a,h)anthracene	6.51	k
Benzo(ghi)perylene	6.90	k

Table F-2. Log K_{ow}s Used for Individual PCB Congeners in the USGS Estimated Water Concentration Calculator Spreadsheet for the 2009 PBT Trends Study.

Individual PCB Congeners Log K_{ow} Ref. g

PCB Congeners IUPAC No.	Log K_{ow}
1	4.46
2	4.69
3	4.69
4	4.65
5	4.97
6	5.06
7	5.07
8	5.07
9	5.06
10	4.84
11	5.28
12,13	5.26
12	5.22
13	5.29
14	5.28
15	5.30
16	5.16
17	5.25
18,20	5.34
18	5.24
19	5.02
20,28	5.62
20	5.57
21,33	5.56
21	5.51
22	5.58
23	5.57
24	5.35
25	5.67
26,29	5.63
26	5.66
27	5.44
28	5.67
29	5.60
30	5.44
31	5.67
32	5.44
33	5.60
34	5.66
35	5.82
36	5.88
37	5.83
38	5.76
39	5.89
40,71	5.82
40	5.66
41	5.69
42	5.76
43	5.75
44,47,65	5.82
44	5.75
45	5.53
46	5.53
47	5.85
48	5.78
49,69	5.95
49	5.85
50,53	5.63
50	5.63
51	5.63
52	5.84
53	5.62
54	5.21
55	6.11
56	6.11
57	6.17
58	6.17
59,62,75	5.96
59	5.95
60	6.11
61,70,74,76	6.14
61	6.04
62	5.89
63	6.17
64	5.95
65	5.86
66	6.20
67	6.20
68	6.26
69	6.04
70	6.20
71	5.98
72	6.26
73	6.04
74	6.20
75	6.05
76	6.13
77	6.36
78	6.35
79	6.42
80	6.48
81	6.36
82	6.20
83	6.26
84	6.04
85,116	6.32

Table F-2. (continued)

PCB Congeners IUPAC No.	Log K_{ow}
85	6.30
86,87,97,108,119,125	6.44
86	6.23
87	6.29
88	6.07
89	6.07
90,101,113	6.43
90	6.36
91	6.13
92	6.35
93,100	6.14
93	6.04
94	6.13
95	6.13
96	5.71
97	6.29
98	6.13
99	6.39
100	6.23
101	6.38
102	6.16
103	6.22
104	5.81
105	6.65
106	6.64
107,124	6.72
107	6.71
108	6.71
109	6.48
110	6.48
111	6.76
112	6.45

PCB Congeners IUPAC No.	Log K_{ow}
113	6.54
114	6.65
115	6.49
116	6.33
117	6.46
118	6.74
119	6.58
120	6.79
121	6.64
122	6.64
123	6.74
124	6.73
125	6.51
126	6.89
127	6.95
128,166	6.84
128	6.74
129,138,163	6.85
129	6.73
130	6.80
131	6.58
132	6.58
133	6.86
134	6.55
135,151	6.64
135	6.64
136	6.22
137	6.83
138	6.83
139,140	6.67
139	6.67
140	6.67

PCB Congeners IUPAC No.	Log K_{ow}
141	6.82
142	6.51
143	6.60
144	6.67
145	6.25
146	6.89
147,149	6.66
147	6.64
148	6.73
149	6.67
150	6.32
151	6.64
152	6.22
153,168	7.02
153	6.92
154	6.76
155	6.41
156,157	7.18
156	7.18
157	7.18
158	7.02
159	7.24
160	6.93
161	7.08
162	7.24
163	6.99
164	7.02
165	7.05
166	6.93
167	7.27
168	7.11
169	7.42

Table F-2. (continued)

PCB Congeners IUPAC No.	Log K_{ow}
170	7.27
171,173	7.07
171	7.11
172	7.33
173	7.02
174	7.11
175	7.17
176	6.76
177	7.08
178	7.14
179	6.73
180,193	7.44
180	7.36
181	7.11
182	7.20
183	7.20
184	6.85
185	7.11
186	6.69
187	7.17
188	6.82
189	7.71
190	7.46
191	7.55
192	7.52
193	7.52
194	7.80
195	7.56
196	7.65
197	7.30
198,199	7.41
198	7.62
199	7.20
200	7.27
201	7.62
202	7.24
203	7.65
204	7.30
205	8.00
206	8.09
207	7.74
208	7.71
209	8.18

Table F-2. (continued)

Individual PBDE Congeners IUPAC No.	Log K_{ow}	Ref.
47	6.22	h, j
49	6.22	f
66	6.25	j
71	6.02	f, j
99	6.75	h, j
100	6.64	h, j
138	7.57	j
153	7.17	h, j
154	7.39	h, j
183	7.71	h, j
184	8.27	f
191	8.36	f, j
209	10.0	j

IUPAC = International Union of Pure and Applied Chemistry; a systematic method of naming organic chemical compounds.

Ref. = Reference.

If multiple log K_{ow} values were found in the literature, a mean value was selected using the t test at 95% confidence for rejection of outliers (USGS 2008 and Alvarez 2008).

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[e] Syracuse Research Corporation, On-Line Log K_{ow} Estimator (KowWin), www.srcinc.com/what-we-do/environment.aspx.

[f] Chlorpyrifos, PBDE-49, -71, -184, and -191 values estimated from Endrin (USGS 2008), PBDE-47, -69, -183, and -190 respectively, due to their proximity in Log K_{ow} values.

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Appendix G. Field Replicate Results

G-1. Field Replicate Residue Accumulated in SPMDs: April – May Spring Deployment, 2009 (ng/5-SPMDs).

Parameter	Lower Columbia		Lower Columbia Replicate		RPD %
p,p'-DDT	10	UJ	11	J	10
p,p'-DDE	47	J	71		41
p,p'-DDD	28	J	44		44
o,p'-DDT	10	UJ	10	U	
o,p'-DDE	10	UJ	10	U	
o,p'-DDD	10	UJ	11		10
DDMU	14	J	19		30
Dieldrin	10	UJ	10		
Chlorpyrifos	93	J	140		40
Endosulfan I	10	J	15		40
Endosulfan-II	10	UJ	32	J	105
Endosulfan Sulfate	10	UJ	10	U	
Hexachlorobenzene (HCB)	18	J	36		67
Pentachloroanisole (PCA)	17	J	28		49
Toxaphene	100	UJ	100	U	
Chlordane (technical)	100	UJ	100	U	
trans-Chlordane	10	UJ	10	U	
cis-Chlordane	10	UJ	10	U	
Dacthal	11	J	16	J	37
trans-Nonachlor	10	UJ	10	U	
cis-Nonachlor	10	UJ	10	U	
Heptachlor	10	UJ	10	U	
Heptachlor Epoxide	10	UJ	10	U	
a-BHC	10	UJ	10	U	
b-BHC	10	UJ	10	U	
d-BHC	10	UJ	10	U	
Lindane	12	J	10	U	18
Aldrin	10	UJ	10	U	
Endrin	10	UJ	10	U	
Endrin ketone	10	UJ	10	U	
Endrin aldehyde	10	UJ	10	U	
Mirex	10	UJ	10	U	
p,p'-Methoxychlor	10	UJ	10	U	
Oxychlordane	10	UJ	10	U	

Table G-1. (continued)

Parameter	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
PBDE-47	20 J	30	40	61	68	11
PBDE-49	1.3 J	2 J	42	2.7 J	3 J	11
PBDE-66	8 UJ	8 U		2 J	8 U	120
PBDE-71	8 UJ	8 U		8 U	8 U	
PBDE-99	12 J	16	29	41	42	2
PBDE-100	2.9 J	4.6 J	45	8.9	11	21
PBDE-138	16 UJ	16 U		16 U	16 U	
PBDE-153	3.2 J	3.5 J	9	4.9 J	5.2 J	6
PBDE-154	16 UJ	5.1 J	103	6 J	5.8 J	3
PBDE-183	3.7 J	3.8 J	3	4.7 J	4.3 J	9
PBDE-184	16 UJ	16 U		16 U	16 U	
PBDE-191	16 UJ	16 U		16 U	16 U	
PBDE-209	40 UJ	40 U		40 U	40 U	

PRC*	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
PCB-004	34	35	2	34.4	34.1	1
PCB-029	128	119	7	128	135	5
PCB-050	156	153	2	159	166	4

*Performance/Permeability Reference Compound.

Table G-1. (continued)

Parameter	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
Naphthalene	180 J	300	50	300	310	3
2-Methylnaphthalene	380 J	640	51	620	660	6
1-Methylnaphthalene	210 J	350	50	320	330	3
2-Chloronaphthalene	40 UJ	40 U		40 U	40 U	
Acenaphthylene	40 UJ	25 J	46	26 J	27 J	4
Acenaphthene	59 J	94	46	31 J	33 J	6
Dibenzofuran	72 J	100	33	75	76	1
Fluorene	56 J	93	50	62	64	3
Phenanthrene	410 J	580	34	350	360	3
Anthracene	40 UJ	40 U		40 U	40 U	
Carbazole	40 UJ	40 U		40 U	40 U	
Fluoranthene	650 J	950	38	740	730	1
Pyrene	350 J	480	31	300	340	13
Retene	480 J	680	34	750	720	4
Benzo(a)anthracene	88 J	100	13	93	98	5
Chrysene	40 UJ	2.8 J	174	40 UJ	5.1 J	155
Benzo(b)fluoranthene	66 J	75	13	69	72	4
Benzo(k)fluoranthene	53 J	54	2	52	52	
Benzo(a)pyrene	39 J	39 J		40	40	
Indeno(1,2,3-cd)pyrene	40 UJ	40 U		40 U	40 U	
Dibenzo(a,h)anthracene	40 UJ	40 U		40 U	40 U	
Benzo(ghi)perylene	40 UJ	40 U		40 U	40 U	

Table G-1. (continued)

Parameter	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
PCB-001	0.488	0.531	8	0.369	0.418	12
PCB-002	0.107	0.121	12	0.088	0.0968	10
PCB-003	0.279	0.287	3	0.244	0.254	4
PCB-004	34.4	35.1	2	34.4	34.1	1
PCB-005	0.0808	0.0823	2	0.0862	0.092	7
PCB-006	0.824	0.855	4	0.648	0.685	6
PCB-007	0.174	0.176	1	0.166	0.186	11
PCB-008	3.65	3.79	4	3.26	3.43	5
PCB-009	0.248	0.247	0	0.23	0.249	8
PCB-010	0.139	0.152	9	0.0754	0.081	7
PCB-011	51.4	54.9	7	3.58	3.94	10
PCB-012/013	0.681	0.689	1	0.331	0.357	8
PCB-014	92.2	97.7	6	85.5	97.1	13
PCB-015	3.04	3.08	1	1.59	1.66	4
PCB-016	2.07	2.02	2	1.79	1.81	1
PCB-017	3.85	4.01	4	2.24	2.43	8
PCB-018/030	6.14	6.26	2	4.48	4.89	9
PCB-019	1.24	1.35	8	0.59	0.648	9
PCB-020/028	9.77	9.25	5	7.71	7.8	1
PCB-021/033	3.58	3.33	7	3.47	3.42	1
PCB-022	2.6	2.45	4	2.2	2.24	1
PCB-023	0.0197 J	0.0175 J	12	0.0185 J	0.0197 J	6
PCB-024	0.105	0.109	4	0.02 U	0.0899	127
PCB-025	1.31	1.38	5	0.585	0.505	15
PCB-026/029	128	119	7	128	135	5
PCB-027	1.02	1.08	6	0.382	0.413	8
PCB-031	9.91	9.34	6	7.61	7.38	3
PCB-032	2.77	2.96	7	1.67	1.83	9
PCB-034	0.0705	0.0677	4	0.0378	0.0339	11
PCB-035	0.33	0.309	7	0.223	0.232	4
PCB-036	0.0878	0.0819	7	0.0545	0.0588	8
PCB-037	1.75	1.74	1	1.39	1.45	4
PCB-038	0.0449	0.0475	6	0.0287	0.0305	6
PCB-039	0.0129 J	0.0157 NJ	20	0.00417 NJ	0.00884 J	72
PCB-040/071	3.64	3.81	5	2.19	2.19	0
PCB-041	0.786	0.741	6	0.67	0.68	1
PCB-042	2.66	2.66	0	1.7	1.69	1

Parameter	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
PCB-043	0.42	0.425	1	0.302	0.301	0
PCB-044/047/065	9.7	9.78	1	5.93	5.94	0
PCB-045	1.83	1.87	2	1.35	1.41	4
PCB-046	0.714	0.724	1	0.486	0.492	1
PCB-048	1.8	1.81	1	1.42	1.45	2
PCB-049/069	6.72	6.69	0	3.96	3.96	0
PCB-050/053	156	153	2	159	166	4
PCB-051	0.693	0.64	8	0.344	0.336	2
PCB-052	10.8	11.2	4	6.96	7.07	2
PCB-054	0.0564	0.0596	6	0.0195 J	0.0222	13
PCB-055	0.112	0.125	11	0.1	0.103	3
PCB-056	1.96	2.1	7	1.33	1.35	1
PCB-057	0.0422	0.0458	8	0.0237 NJ	0.0242	2
PCB-058	0.0203	0.0194 J	5	0.0104 NJ	0.00971 J	7
PCB-059/062/075	0.843	0.855	1	0.55	0.548	0
PCB-060	1.37	1.46	6	0.893	0.892	0
PCB-061/070/074/076	8.37	8.84	5	6.38	6.33	1
PCB-063	0.253	0.278	9	0.139	0.135	3
PCB-064	3.91	4.06	4	2.29	2.31	1
PCB-066	5.0	5.23	6	3.4	3.39	1
PCB-067	0.171	0.178	4	0.123	0.117	5
PCB-068	0.161	0.165	2	0.136	0.142	4
PCB-072	0.0751	0.0812	8	0.0296	0.0303	2
PCB-073	0.18	0.169	6	0.124	0.128	3
PCB-077	0.368	0.375	2	0.229	0.243	6
PCB-078	89.1	93.6	5	89.5	91.5	2
PCB-079	0.0435	0.0484	11	0.0286	0.0251	13
PCB-080	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-081	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-082	0.504	0.503	0	0.362	0.399	10
PCB-083	0.301	0.263	13	0.231	0.261	12
PCB-084	1.75	1.72	2	1.18	1.21	3
PCB-085/116	0.822	0.8	3	0.578	0.655	12
PCB-086/087/097/108/119/125	3.27	3.23	1	2.31	2.51	8
PCB-088	0.0152 J	0.02 U	27	0.0132 J	0.0158 NJ	18
PCB-089	0.153	0.151	1	0.113	0.117	3
PCB-090/101/113	5.9	5.79	2	4.33	4.69	8
PCB-091	0.818	0.816	0	0.514	0.528	3

Parameter	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
PCB-092	1.11	1.11	0	0.802	0.835	4
PCB-093/100	0.216	0.203	6	0.148	0.152	3
PCB-094	0.0563	0.051	10	0.0257	0.023 NJ	11
PCB-095	5.95	5.71	4	4.17	4.32	4
PCB-096	0.0741	0.0834	12	0.0446	0.0472	6
PCB-098	0.0442	0.0487	10	0.0351 NJ	0.0387	10
PCB-099	2.03	2.08	2	1.39	1.48	6
PCB-102	0.277	0.267	4	0.154	0.165	7
PCB-103	0.0712	0.0727	2	0.0464	0.0465	0
PCB-104	0.0109 J	0.00682 NJ	46	0.00969 J	0.0048 NJ	67
PCB-105	1.21	1.26	4	0.892	0.954	7
PCB-106	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-107/124	0.135	0.137	1	0.0958	0.104	8
PCB-109	0.236	0.248	5	0.148	0.165	11
PCB-110	4.5	4.9	8	3.2	3.47	7
PCB-111	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-112	0.022	0.0181 J	19	0.0153 J	0.02 U	27
PCB-114	0.0789	0.0824	4	0.0557	0.0597	7
PCB-115	0.45	0.114	119	0.0324	0.0866	91
PCB-117	0.138	0.155	12	0.0911	0.0979	7
PCB-118	2.98	3.1	4	1.96	2.1	5
PCB-120	0.0156 J	0.0166 J	6	0.00798 NJ	0.00933 J	16
PCB-121	0.01 J	0.0109 J	9	0.00809 J	0.008 J	1
PCB-122	0.0529	0.0525	1	0.0424	0.0416	2
PCB-123	0.0564	0.0618	9	0.0481	0.0466 NJ	3
PCB-126	0.0364	0.0372	2	0.0329	0.0328	0
PCB-127	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-128/166	0.358	0.372	4	0.302	0.352	15
PCB-129/138/163	2.58	2.65	3	2.19	2.41	10
PCB-130	0.199	0.208	4	0.165	0.193	16
PCB-131	0.0356	0.0339	5	0.0314	0.0349	11
PCB-132	0.883	0.863	2	0.79	0.882	11
PCB-133	0.0487	0.0517	6	0.0406	0.0417	3
PCB-134	0.219	0.218	0	0.161	0.191	17
PCB-135/151	1.7	1.51	11	1.6	1.7	8
PCB-136	0.541	0.538	1	0.524	0.548	4
PCB-137	0.0774	0.0768	1	0.0668	0.0783	16
PCB-139/140	0.0476	0.0448	6	0.0399	0.0432	8

Parameter	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
PCB-141	0.443	0.448	1	0.492	0.531	8
PCB-142	0.0313	0.0273	14	0.0294	0.0355 NJ	19
PCB-143	0.0964	0.0818	16	0.11	0.116	5
PCB-144	0.208	0.188	10	0.198	0.218	10
PCB-145	0.131	0.114	14	0.123	0.157	24
PCB-146	0.41	0.415	1	0.334	0.365	9
PCB-147/149	2.95	2.76	7	2.57	2.88	11
PCB-148	0.0082 J	0.00659 J	21	0.02 U	0.00412 J	132
PCB-150	0.0044 J	0.00466 J	5	0.02 U	0.00261 NJ	154
PCB-152	0.179	0.156	14	0.176	0.178	1
PCB-153/168	2.23	2.26	1	1.81	1.99	9
PCB-154	0.0551	0.054	2	0.0326	0.0353	8
PCB-155	0.009 J	0.00886 J	2	0.00933 J	0.0101 J	8
PCB-156/157	0.187	0.196	5	0.175	0.2	13
PCB-158	0.219	0.216	1	0.195	0.218	11
PCB-159	0.021	0.0213	1	0.0244	0.0239	2
PCB-160	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-161	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-162	0.0063 J	0.00682 J	8	0.00403 J	0.02 U	133
PCB-164	0.162	0.171	5	0.153	0.18	16
PCB-165	0.0036 J	0.02 U	139	0.02 U	0.02 U	
PCB-167	0.0846	0.0873	3	0.0646	0.079	20
PCB-169	0.0163 J	0.0122 NJ	29	0.014 J	0.016 J	13
PCB-170	0.225	0.22	2	0.249	0.284	13
PCB-171/173	0.11	0.104	6	0.106	0.109	3
PCB-172	0.0501 NJ	0.0523 NJ	4	0.0659	0.0635	4
PCB-174	0.382	0.381	0	0.437	0.449	3
PCB-175	0.0337	0.0319	5	0.0315	0.0394	22
PCB-176	0.077	0.0743	4	0.0844	0.093	10
PCB-177	0.231	0.224	3	0.221	0.231	4
PCB-178	0.136	0.136	0	0.141	0.153	8
PCB-179	0.314	0.302	4	0.325	0.347	7
PCB-180/193	0.59	0.583	1	0.66	0.746	12
PCB-181	0.0133 J	0.00939 NJ	34	0.0113 J	0.00689 NJ	48
PCB-182	0.02 U	0.02 U		0.02 U	0.02 U	
PCB-183	0.283	0.295	4	0.291	0.321	10
PCB-184	0.0025 NJ	0.00321 NJ	26	0.00391 NJ	0.00477 NJ	20
PCB-185	0.0546	0.0519	5	0.0589	0.059	0

Parameter	Lower Columbia	Lower Columbia Replicate	RPD %	Spokane at Nine Mile Dam	Spokane at Nine Mile Dam Replicate	RPD %
PCB-186	82.7	83	0	80.7	82.3	2
PCB-187	0.708	0.723	2	0.686	0.733	7
PCB-188	0.0027 J	0.02 U	152	0.02 U	0.02 U	
PCB-189	0.0093 J	0.00858 J	8	0.00913 NJ	0.0155 NJ	52
PCB-190	0.0587	0.0575	2	0.0574	0.0649	12
PCB-191	0.011 J	0.0119 J	8	0.0144 J	0.0138 J	4
PCB-192	0.0038 NJ	0.02 U	136	0.02 U	0.02 U	
PCB-194	0.0632	0.0567	11	0.0715	0.0836	16
PCB-195	0.0438	0.0367	18	0.0474	0.0473	0
PCB-196	0.0456	0.0412	10	0.0555	0.0632	13
PCB-197	0.008 J	0.00764 J	4	0.00821 J	0.0101 J	21
PCB-198/199	0.124	0.111	11	0.151	0.185	20
PCB-200	0.0245	0.0244	0	0.0271 NJ	0.0371	31
PCB-201	0.0405	0.0396	2	0.0437	0.0503	14
PCB-202	0.0596	0.0568	5	0.062	0.063	2
PCB-203	0.0619	0.0574	8	0.0731	0.0769	5
PCB-204	0.0647	0.0681	5	0.0675	0.0673	0
PCB-205	0.0064 NJ	0.0068 J	6	0.00693 J	0.0123 J	56
PCB-206	0.0449	0.0394	13	0.0476	0.0757	46
PCB-207	0.009 J	0.00857 J	5	0.00843 J	0.0143 J	52
PCB-208	0.0165 J	0.015 NJ	10	0.0208	0.0181 NJ	14
PCB-209	0.0691	0.115	50	0.0752	0.149	66

J = estimated concentration.
U = not detected at or above reported result.
UJ = not detected at or above reported estimated result.
NJ = analyte identified as estimate.

Appendix H. Streamflow Data

Table H-1. Flow Data for the 2009 PBT Trends Study, Spring.

Site	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Lower Columbia River	54	USGS	14246900	Columbia River at Beaver Army Terminal near Quincy, OR	4/29/09 - 5/27/09	271,000-407,000	345,662.9
Middle Columbia River	292[a]	USACE & USGS	McNary & 14019200	Columbia River at McNary Dam near Umatilla, OR	4/30/09 - 5/28/09	188,500-341,300	253,177.7
Upper Columbia River	453.5	USGS	12462600	Columbia River below Rock Island Dam, WA	4/28/09 - 5/26/09	59,420-152,420	120,124.1
Queets River	11.5[b]	USGS	12040500	Queets River near Clearwater, WA	5/4/09 - 6/1/09	1,586-6,029	2,411.0
Yakima River	18	USGS	12510500	Yakima River at Kiona, WA	4/30/09 - 5/28/09	2,940-11,800	6,302.9
Walla Walla River	9	USGS	14018500	Walla Walla River near Touchet, WA	4/30/09 - 5/28/09	1,060-3,640	1,832.6
Spokane River	58.1[c]	USGS & Spokane	12422500	Spokane River at Spokane, WA	4/30/09 - 5/28/09	16,102-22,007	19,092.7
			12424000	Hangman Creek at Spokane, WA			
			City of Spokane 2008	RPWRF Spokane WWTP			
Lake Washington	na	King Co.	King County, 2005	Controlled water level: fluctuation ~ 2 ft	4/28/09 - 5/26/09	Flushing Rate 0.43 / year	--

USACE = U.S. Army Corps of Engineers.
RPWRF = Riverside Park Water Reclamation Facility.

[a] Flow for the McNary site was the Outflow Discharge.

[b] Flow for the Queets site was calculated by subtracting the Clearwater River percent contribution (23%) from the Queets River flow data based on available historical data for the Queets River above Clearwater.

[c] Flow for the Spokane site was the sum discharge from Spokane River, Hangman Creek, and the Spokane Wastewater Treatment Plant (WWTP). Historical (1995-2009) WWTP contribution ranged from .44-5.27%.

Table H-2. Flow Data for the 2009 PBT Trends Study, Fall.

Site Location	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Spokane River	58.1[a]	USGS & Spokane	12422500	Spokane River at Spokane, WA	9/3/08 - 9/30/09	881-1,524	1,300.3
			12424000	Hangman Creek at Spokane, WA			
			City of Spokane 2008	RPWRF Spokane WWTP			
Spokane River	98.3	USGS	12419000	Spokane River near the Idaho border	9/3/08 - 9/30/09	496-1,248	1,036.8

RPWRF = Riverside Park Water Reclamation Facility.

a. Flow for the Spokane site was the sum discharge from Spokane River, Hangman Creek, and the Spokane Wastewater Treatment Plant (WWTP). Historical (1995-2009) WWTP contribution ranged from .44-5.27%.

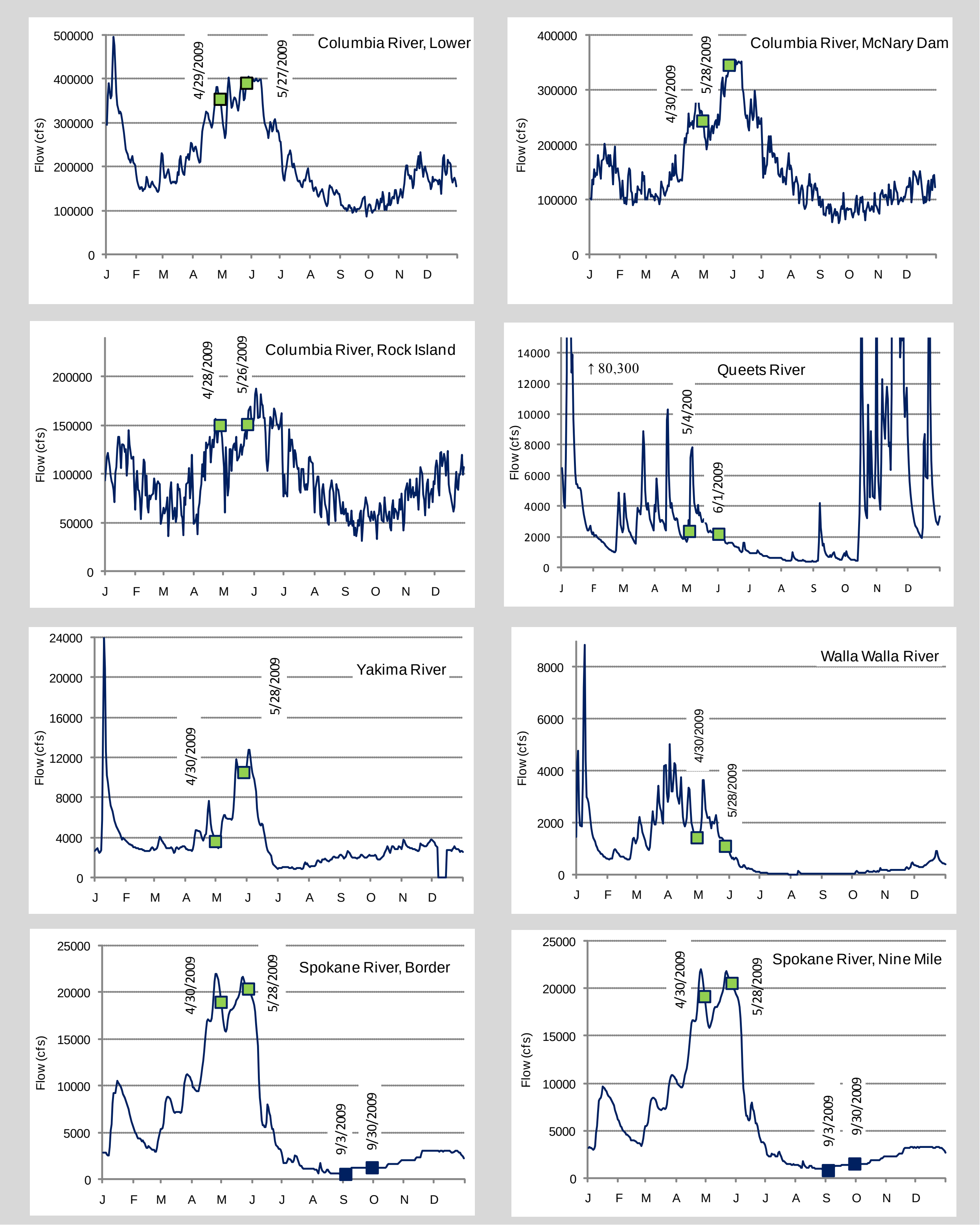

Figure H-1. Flow Charts and Sampling Dates for the 2009 PBT Trends Study.

Appendix I. Ancillary Water Quality Data

Table I-1. Ancillary Water Quality Data, Spring 2009.

Site	Field ID	Sample Number	Collection Date	Conductivity (uS/cm)	TSS (mg/L)	TOC (mg/L)
Lower Columbia River	LCR	90503301	4/29/2009	133	15	2.1
	LCR	90504701	5/11/2009	119	25 J	1.7
	LCR	90505901	5/27/2009	126	27	2.0
Middle Columbia River at McNary Dam	MCNARY	90503302	4/30/2009	159	6	1.8
	MCNARY	90504702	5/13/2009	142	6	1.9
	MCNARY	90504902	5/28/2009	121	8	1.9
Upper Columbia River at Rock Island Dam	ROCK	90503303	4/28/2009	132	4	1.2
	ROCK	90504703	5/13/2009	132	5	1.4
	ROCK	90505903	5/26/2009	72	5	1.6
Queets River	QUEETS	90503304	5/4/2009	64	12	1.0
	QUEETS	90504704	5/15/2009	64	13	1.0 U
	QUEETS	90505904	6/1/2009	61	18	1.0 U
Yakima River at Wanawish Dam	YAK	90503305	4/30/2009	178	18	2.9
	YAK	90504705	5/13/2009	134	51	2.0
	YAK	90505905	5/28/2009	99	98	1.6
Walla Walla River	WALLA	90503306	4/30/2009	115	101	2.5
	WALLA	90504706	5/13/2009	82	125	5.7
	WALLA	90505906	5/28/2009	99	62	1.6
Spokane River at Nine Mile Dam	SPOK	90503307	4/30/2009	62	8	1.9
	SPOK	90504707	5/14/2009	67	7	1.7
	SPOK	90505907	5/28/2009	51	6	1.5
Lake Washington	WASH	90503308	4/28/2009	90	3	2.4
	WASH	90504708	5/12/2009	93	2	1.9
	WASH	90505908	5/26/2009	98	3	2.4

U = Not detected at or above reported quantitation limit.
Mean estimated using detection limit (1.0) for nondetects.

Table I-2. Ancillary Water Quality Data, Fall 2009.

Site	Field ID	Sample Number	Collection Date	Conduct. (us/cm)	TSS (mg/L)	TOC (mg/L)
Spokane River at Nine Mile Dam	SPOK	91002607	9/3/2009	276	2	1.0 U
	SPOK	91002607	9/21/2009	218	2	1.2
	SPOK	91002607	9/30/2009	215	2	1.3
Spokane River near Idaho Border	SPOKBD	91002643	9/3/2009	49	1 U	1.5
	SPOKBD	91002643	9/17/2009	50	1 U	1.3
	SPOKBD	91002643	9/30/2009	48	1 U	1.7

U = Not detected at or above reported quantitation limit.
Mean estimated using detection limit (1.0) for nondetects.

Appendix J. Estimated Dissolved Concentrations in SPMDs, 2009

Table J-1. Estimated Concentration of Pesticides and Total PCBs Detected in SPMDs, April - May 2009 (pg/L).

Parameter	Lower Columbia River	Middle Columbia River	Upper Columbia River	Queets River	Yakima River	Walla Walla River	Spokane River at Nine Mile Dam	Lake Washington	Replicate	
									Lower Columbia River	Spokane River
Sample #:	0906043-01	0906043-02	0906043-03	0906043-04	0906043-05	0906043-06	0906043-07	0906043-08	0906043-13	0906043-14
4,4'-DDT	6.4 UJ	4.1 U	12 J	13 U	18 J	43 J	- -	- -	6.7 J	- -
4,4'-DDE	32 J	12	78	15 U	180	160	- -	- -	46	- -
4,4'-DDD	18 J	9.0	85	13 U	40	33	- -	- -	26	- -
2,4'-DDT	6.4 UJ	4.0 U	7.6 U	13 U	5.8 U	9.8 J	- -	- -	6.0 U	- -
2,4'-DDE	6.4 UJ	4.0 U	7.6 U	13 U	5.8 U	7.0 U	- -	- -	6.0 U	- -
2,4'-DDD	6.8 UJ	4.0 U	23	15 U	8.6	12 J	- -	- -	7.0	- -
Total DDT[1]	50 J	22	200	nd	240	260 J	- -	- -	86	- -
DDMU[2]	9.0 J	4.1 U	25	13 U	11 J	34 UJ	- -	- -	12	- -
Dieldrin	11 UJ	9.7 U	12 U	18 U	37	26 J	- -	- -	11	- -
Chlorpyriphos	200 J	110	100	25 U	1000	6600	- -	- -	300	- -
Endosulfan I	220 J	220 U	530	220 U	2200 J	410 J	- -	- -	330	- -
Endosulfan II	460 UJ	460 U	460 U	460 U	970	580 U	- -	- -	1500 J	- -
Endosulfan Sulfate	320 UJ	320 U	320 U	320 U	440	400 U	- -	- -	320 U	- -
Hexachlorobenzene	11 J	3.9 U	14	13 U	7.6	46	- -	- -	22	- -
Pentachloroanisole	11 J	4.1 U	7.7 U	13 U	12	20	- -	- -	17	- -
Toxaphene	98 UJ	79 U	110 U	160 U	190 J	1000 J	- -	- -	95 U	- -
Total Chlordane[3]	7.5 UJ	4.3 U	9.1 U	16 U	6.8 U	34 J	- -	- -	7.0 U	- -
Dacthal (DCPA)	22 J	20	21 U	26 U	27 J	74 J	- -	- -	31 J	- -
Heptachlor Epoxide	13 UJ	11 U	14 U	20 U	12 U	15 U	- -	- -	13 U	- -
Gamma-BHC (Lindane)	82 J	68 U	68 U	72 U	68 U	85 U	- -	- -	68 U	- -
Total PCBs	130	5.4	44	42	64	45	70	56	130	82

See next page

Notes for Table J-1:

1. Total DDT is the sum of 2,4'- and 4,4' isomers of DDD, DDE, and DDT.
   DDD = p,p'-dichlorodiphenyldichloroethane. DDE = p,p'-dichlorodiphenyldichloroethylene. DDT = p,p'-dichlorodiphenyltrichloroethane.
2. DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.
3. The NTR criterion for chlordane is interpreted as the sum of five chlordane components: Total chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane.

J = The analyte was positively identified. The associated numerical result is an estimate.
U = The analyte was not detected at or above the reported value.
UJ = The analyte was not detected at or above the reported estimated results.
nd = not detected.
- = not analyzed.

Table J-2. Estimated Concentration of PBDEs Detected in SPMDs, April - May 2009 (pg/L).

Parameter	Lower Columbia River	Middle Columbia River	Upper Columbia River	Queets River	Yakima River	Walla Walla River	Spokane River at Nine Mile Dam	Lake Washington	Replicate	
									Lower Columbia River	Spokane River
Sample #:	0906043-01	0906043-02	0906043-03	0906043-04	0906043-05	0906043-06	0906043-07	0906043-08	0906043-13	0906043-14
PBDE-047	4.2 JK	- -	- -	22 UJK	21 JK	- -	34 JK	5.1 JK	11 JK	44 JK
PBDE-049	0.9 UJK	- -	- -	12 U	2.8 UJK	- -	2.0 UJK	5.1 U	1.3 UJK	2.4 UJK
PBDE-066	5.7 U	- -	- -	12 U	1.7 UJK	- -	1.5 UJK	5.2 U	5.4 U	6.5 U
PBDE-071	5.4 U	- -	- -	12 U	4.9 U	- -	5.5 U	4.8 U	5.0 U	6.0 U
PBDE-099	11 UJK	- -	- -	24 UJK	11 JK	- -	27 JK	15 UJK	14 UJK	31 JK
PBDE-100	2.5 UJK	- -	- -	4.9 UJK	3.2 JK	- -	5.5 JK	1.4 JK	1.6 JK	8.2 JK
PBDE-138	25 U	- -	- -	56 U	22 U	- -	26 U	22 U	23 U	28 U
PBDE-153	3.8 UJK	- -	- -	7.9 UJK	4.2 UJK	- -	1.6 JK	4.0 UJK	3.8 UJK	2.1 JK
PBDE-154	22 U	- -	- -	15 UJK	7.0 UJK	- -	8.4 UJK	6.2 UJK	6.5 UJK	9.1 UJK
PBDE-183	6.4 UJK	- -	- -	14 UJK	6.7 UJK	- -	8.4 UJK	6.2 UJK	6.2 UJK	8.5 UJK
PBDE-184	43 U	- -	- -	96 U	38 U	- -	44 U	38 U	40 U	49 U
Total PBDEs	4.2 JK	- -	- -	nd	35 JK	- -	69 JK	6.4 JK	12 JK	85 JK

U = The analyte was not detected at or above the reported result.
JK = The analyte was positively identified. Reported result is an estimate with unknown bias.
UJK = The analyte was not detected at or above the reported estimate with unknown bias.
nd = not detected.
- = not analyzed.

Table J-3. Estimated Concentration of PAHs Detected in SPMDs, April - May 2009 (pg/L).

Parameter	Lower Columbia River	Middle Columbia River	Upper Columbia River	Queets River	Yakima River	Walla Walla River	Spokane River at Nine Mile Dam	Lake Washington	Replicate	
									Lower Columbia River	Spokane River
Sample #:	0906043-01	0906043-02	0906043-03	0906043-04	0906043-05	0906043-06	0906043-07	0906043-08	0906043-13	0906043-14
Naphthalene	2400 UJK	1500 UJK	3000 UJK	2800 UJK	2900 UJK	3100 UJK	1800 JK	2600 JK	1800 JK	1900 JK
2-Methylnaphthalene	1800 UJK	1000 UJK	970 JK	1800 UJK	770 JK	2000 UJK	1700 JK	2900 JK	1800 JK	1900 JK
1-Methylnaphthalene	380 JK	600 UJK	570 JK	880 UJK	420 JK	1200 UJK	890 JK	1600 JK	1000 JK	940 JK
2-Chloronaphthalene	210 U	210 U	210 U	230 U	210 U	260 U	210 U	210 U	210 U	210 U
Acenaphthylene	110 U	26 UJK	64 UJK	140 U	110 U	140 U	74 UJK	130	70 UJK	77 UJK
Acenaphthene	120 J	28 UJK	53 UJK	110 U	110	98 UJK	66 UJK	200	200	72 UJK
Dibenzofuran	90 JK	96 UJK	90 JK	110 UJK	130 JK	110 JK	98 JK	140 JK	160 JK	100 JK
Fluorene	89 J	35 UJK	79	90 U	93	97	99	180	140	100
Phenanthrene	460 JK	130 JK	410 JK	110 JK	480 JK	440 JK	380 JK	460 JK	690 JK	410 JK
Anthracene	50 U	43 U	54 U	76 U	48 U	59 U	50 U	48 U	48 U	52 U
Carbazole	1000 U	1000 U	1000 U	1000 U	1000 U	1300 U	1000 U	1000 U	1000 U	1000 U
Fluoranthene	400 JK	56 JK	315 JK	25 JK	200 JK	190 JK	470 JK	720 JK	580 JK	500 JK
Pyrene	230 J	16 UJK	62	14 UJK	99	120	200	500	300	250
Retene	360 J	56 J	290	72	200	140	570	64	480	610
Benzo(a)anthracene	26 JK	26 UJK	54 UJK	89 UJK	44 UJK	51 UJK	30 JK	66 JK	32 JK	37 JK
Chrysene	26 U	16 U	30 U	53 U	23 U	28 U	26 U	220	1.7 UJK	3.6 UJK
Benzo(b)fluoranthene	15 JK	20 UJK	8.0 JK	54 U	9.0 JK	8.6 JK	17 JK	150 JK	20 JK	21 JK
Benzo(k)fluoranthene	7.5 JK	20 UJK	41 UJK	61 U	31 UJK	36 UJK	6.9 JK	43 JK	7.6 JK	7.7 JK
Benzo(a)pyrene	29 UJK	15 UJK	34 UJK	66 U	25 UJK	30 UJK	31 UJK	15 JK	27 UJK	34 UJK
Indeno(1,2,3-cd)pyrene	36 U	20 U	44 U	81 U	33 U	39 U	37 U	32 UJK	34 U	41 U
Dibenzo(a,h)anthracene	32 U	18 U	39 U	71 U	29 U	34 U	33 U	29 U	30 U	36 U
Benzo(ghi)perylene	40 U	22 U	49 U	88 U	36 U	42 U	41 U	26 UJK	37 U	45 U
Total LPAH[1]	680 JK	130 JK	490 JK	110 JK	680 JK	540 JK	2300 JK	3600 JK	2800 JK	2400 JK
Total HPAH[2]	680 JK	56 JK	380 JK	25 JK	310 JK	320 JK	730 JK	1700 JK	940 JK	820 JK
Total PAH[3]	1400 JK	180 JK	870 JK	130 JK	990 JK	860 JK	3000 JK	5300 JK	3800 JK	3200 JK

Notes for Table J-3:

1. Total LPAH is the sum of low molecular weight PAHs: naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, and fluorene.
2. Total HPAH is the sum of high molecular weight PAHs: fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.
3. Total PAH is the sum of LPAH and HPAH.

U = The analyte was not detected at or above the reported result.

JK = The analyte was positively identified. Reported result is an estimate with unknown bias.

UJK = The analyte was not detected at or above the reported estimate with unknown bias.

Table J-4. Estimated Concentration of Total PCBs and PBDEs Detected in SPMDs, September 2009 (pg/L).

Parameter	Spokane River at Nine Mile Dam		Spokane River at Idaho Border	
Sample No.	0910026-07		0910026-43	
Total PCBs	83		46	
PBDE-047	140	JK	24	JK
PBDE-049	4.5		2.5	U
PBDE-066	2.7		2.5	U
PBDE-071	2.4	U	2.3	U
PBDE-099	80	JK	7.1	JK
PBDE-100	18	JK	2.4	JK
PBDE-138	2.3	UJK	11	U
PBDE-153	5.5	UJK	8.1	U
PBDE-154	4.1	JK	3.2	UJK
PBDE-183	3.8	UJK	3.1	UJK
PBDE-184	19	U	18	U
Total PBDEs	240		33	

U = The analyte was not detected at or above the reported result.
JK = The analyte was positively identified. Reported result is an estimate with unknown bias.
UJK = The analyte was not detected at or above the reported estimate with unknown bias.

Appendix K. Estimated Total Concentrations in SPMDs, 2009

Table K-1. Estimated Total Concentration of Pesticides and Total PCBs, April – May 2009 (pg/L).

Parameter	Lower Columbia River	Middle Columbia River	Upper Columbia River	Queets River	Yakima River	Walla Walla River	Spokane River at Nine Mile Dam	Lake Washington	Replicate	
									Lower Columbia River	Spokane River
Sample #:	0906043-01	0906043-02	0906043-03	0906043-04	0906043-05	0906043-06	0906043-07	0906043-08	0906043-13	0906043-14
4,4'-DDT	8.0 UJ	7.9 U	14 J	15 U	22 J	60 J	- -	- -	8.3 J	- -
4,4'-DDE	68 J	66	140	24 U	390	470	- -	- -	96	- -
4,4'-DDD	26 J	25	110	16 U	60	57	- -	- -	38	- -
2,4'-DDT	8.4 UJ	8.8 U	9.3 U	15 U	7.9 U	15 J	- -	- -	7.9 U	- -
2,4'-DDE	8.2 UJ	8.6 U	9.2 U	15 U	7.8 U	10 U	- -	- -	7.8 U	- -
2,4'-DDD	13 UJ	19 U	39	22 U	18	32 J	- -	- -	14	- -
Total DDT[1]	94 J	91	300	nd	490	630 J	- -	- -	160	- -
DDMU[2]	11 J	8.1 U	30	15 U	14 J	48 UJ	- -	- -	14	- -
Dieldrin	12 UJ	11 U	13 U	18 U	39	27 J	- -	- -	11	- -
Chlorpyriphos	210 J	140	100	26 U	1100	7300	- -	- -	310	- -
Endosulfan I	220 J	230 U	530	220 U	2200 J	420 J	- -	- -	330	- -
Endosulfan II	460 UJ	470 U	460 U	460 U	970	580 U	- -	- -	1500 J	- -
Endosulfan Sulfate	320 UJ	320 U	320 U	320 U	450	400 U	- -	- -	320 U	- -
Hexachlorobenzene	16 J	10 U	18	16 U	11	77	- -	- -	30	- -
Pentachloroanisole	14 J	8.0 U	9.0 U	15 U	16	29	- -	- -	21	- -
Toxaphene	100 UJ	92 U	110 U	170 U	200 J	1100 J	- -	- -	99 U	- -
Total Chlordane[3]	7.5 UJ	4.3 U	9.1 U	16 U	6.8 U	34 J	- -	- -	7.0 U	- -
Dacthal (DCPA)	22 J	22	21 U	26 U	27 J	76 J	- -	- -	31 J	- -
Heptachlor Epoxide	14 UJ	17 U	15 U	21 U	14 U	18 U	- -	- -	14 U	- -
Gamma-BHC (Lindane)	82 J	69 U	69 U	72 U	68 U	86 U	- -	- -	68 U	- -
Total PCBs	340	84	130	91	340	330	230	250	340	310

See next page

Notes for Table K-1:

1. Total DDT is the sum of 2,4'- and 4,4' isomers of DDD, DDE, and DDT.
   DDD = p,p'-dichlorodiphenyldichloroethane. DDE = p,p'-dichlorodiphenyldichloroethylene. DDT = p,p'-dichlorodiphenyltrichloroethane.
2. DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.
3. The NTR criterion for chlordane is interpreted as the sum of five chlordane components: Total chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane.

J = The analyte was positively identified. The associated numerical result is an estimate.
U = The analyte was not detected at or above the reported value.
UJ = The analyte was not detected at or above the reported estimated results.
- = not analyzed.

Table K-2. Estimated Total Concentration of PBDEs, April – May 2009 (pg/L).

Parameter	Lower Columbia River	Middle Columbia River	Upper Columbia River	Queets River	Yakima River	Walla Walla River	Spokane River at Nine Mile Dam	Lake Washington	Replicate	
									Lower Columbia River	Spokane River
Sample #:	0906043-01	0906043-02	0906043-03	0906043-04	0906043-05	0906043-06	0906043-07	0906043-08	0906043-13	0906043-14
PBDE-047	9.8 JK	- -	- -	36 UJK	52 JK	- -	74 JK	13 JK	25 JK	94 JK
PBDE-049	2.1 UJK	- -	- -	21 U	6.9 UJK	- -	4.2 UJK	13 U	3.1 UJK	5.2 UJK
PBDE-066	14 U	- -	- -	22 U	4.4 UJK	- -	3.3 UJK	14 U	13 U	15 U
PBDE-071	9.8 U	- -	- -	16 U	9.4 U	- -	9.5 U	9.4 U	9.2 U	10 U
PBDE-099	60 UJK	- -	- -	80 UJK	66 JK	- -	130 JK	90 UJK	74 UJK	150 JK
PBDE-100	11 UJK	- -	- -	14 UJK	16 JK	- -	22 JK	6.8 JK	7.0 JK	33 JK
PBDE-138	760 U	- -	- -	920 U	770 U	- -	690 U	780 U	710 U	770 U
PBDE-153	48 UJK	- -	- -	56 UJK	60 UJK	- -	18 JK	58 UJK	49 UJK	24 JK
PBDE-154	450 U	- -	- -	170 UJK	160 UJK	- -	150 UJK	150 UJK	130 UJK	160 UJK
PBDE-183	270 UJK	- -	- -	320 UJK	310 UJK	- -	310 UJK	300 UJK	260 UJK	310 UJK
PBDE-184	6400 U	- -	- -	7500 U	6400 U	- -	5800 U	6500 U	6000 U	6400 U
Total PBDEs	9.8 JK	- -	- -	nd	130 JK	- -	250 JK	20 JK	32 JK	300 JK

U = The analyte was not detected at or above the reported result.
JK = The analyte was positively identified. Reported result is an estimate with unknown bias.
UJK = The analyte was not detected at or above the reported estimate with unknown bias.
nd = not detected.
- = not analyzed.

Table K-3. Estimated Total Concentrations of PAHs, April – May 2009 (pg/L).

Parameter	Lower Columbia River	Middle Columbia River	Upper Columbia River	Queets River	Yakima River	Walla Walla River	Spokane River at Nine Mile Dam	Lake Washington	Replicate	
									Lower Columbia River	Spokane River
Sample #:	0906043-01	0906043-02	0906043-03	0906043-04	0906043-05	0906043-06	0906043-07	0906043-08	0906043-13	0906043-14
Naphthalene	2500 UJK	1500 UJK	3000 UJK	2800 UJK	2900 UJK	3100 UJK	1800 JK	2600 JK	1800 JK	1900 JK
2-Methylnaphthalene	1800 UJK	1000 UJK	970 JK	1800 UJK	780 JK	2000 UJK	1700 JK	2900 JK	1800 JK	1900 JK
1-Methylnaphthalene	380 JK	620 UJK	570 JK	880 UJK	420 JK	1200 UJK	900 JK	1600 JK	1000 JK	950 JK
2-Chloronaphthalene	210 U	220 U	210 U	230 U	210 U	270 U	210 U	210 U	210 U	210 U
Acenaphthylene	110 U	27 UJK	64 UJK	140 U	110 U	140 U	74 UJK	140	71 UJK	78 UJK
Acenaphthene	130 J	30 UJK	54 UJK	110 U	110	100 UJK	67 UJK	200	200	72 UJK
Dibenzofuran	91 JK	100 UJK	91 JK	110 UJK	130 JK	120 JK	99 JK	140 JK	160 JK	100 JK
Fluorene	90 J	37 UJK	80	91 U	95	100	100	190	150	110
Phenanthrene	480 JK	140 JK	420 JK	110 JK	490 JK	460 JK	390 JK	480 JK	700 JK	420 JK
Anthracene	21 U	48 U	55 U	77 U	49 U	61 U	51 U	49 U	50 U	54 U
Carbazole	1000 U	1000 U	1000 U	1000 U	1000 U	1300 U	1000 U	1000 U	1000 U	1000 U
Fluoranthene	450 JK	84 JK	340 JK	26 JK	230 JK	230 JK	530 JK	830 JK	650 JK	560 JK
Pyrene	270 J	27 UJK	69	16 UJK	120	150	230	590	350	290
Retene	1000 J	440 J	670	140	590	580	1500	190	1300	1600
Benzo(a)anthracene	43 JK	91 UJK	80 UJK	120 UJK	76 UJK	100 UJK	48 JK	120 JK	53 JK	58 JK
Chrysene	34 U	36 U	38 U	62 U	32 U	43 U	34 U	310	2.2 UJK	4.7 UJK
Benzo(b)fluoranthene	22 JK	56 UJK	11 JK	68 U	14 JK	16 JK	25 JK	230 JK	29 JK	30 JK
Benzo(k)fluoranthene	17 JK	120 UJK	79 UJK	100 U	76 UJK	110 UJK	15 JK	100 JK	17 JK	16 JK
Benzo(a)pyrene	81 UJK	120 UJK	77 UJK	120 U	75 UJK	120 UJK	78 UJK	46 JK	76 UJK	87 UJK
Indeno(1,2,3-cd)pyrene	199 U	380 U	190 U	270 U	200 U	330 U	180 U	200 UJK	180 U	200 U
Dibenzo(a,h)anthracene	110 U	200 U	110 U	160 U	110 U	180 U	110 U	110 U	110 U	120 U
Benzo(ghi)perylene	290 U	570 U	270 U	380 U	290 U	490 U	270 U	210 UJK	270 U	300 U
Total LPAH[1]	700 JK	140 JK	500 JK	110 JK	690 JK	560 JK	2300 JK	3600 JK	2800 JK	2400 JK
Total HPAH[2]	800 JK	84 JK	420 JK	26	360 JK	400 JK	850 JK	2200 JK	1100 JK	950 JK
Total PAH[3]	1500 JK	220 JK	920 JK	140 JK	1000 JK	960 JK	3100 JK	5800 JK	3900 JK	3400 JK

Notes for Table K-3:

1. Total LPAH is the sum of low molecular weight PAHs: naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, and fluorene.
2. Total HPAH is the sum of high molecular weight PAHs: fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.
3. Total PAH is the sum of LPAH and HPAH.

U = The analyte was not detected at or above the reported result.
JK = The analyte was positively identified. Reported result is an estimate with unknown bias.
UJK = The analyte was not detected at or above the reported estimate with unknown bias.

Table K-4. Estimated Total Concentrations of Total PCBs and PBDEs, September 2009 (pg/L).

Parameter	Spokane River at Nine Mile Dam		Spokane River at Idaho Border	
Sample No.	0910026-07		0910026-43	
Total PCBs	200		120	
PBDE-047	240	JK	49	JK
PBDE-049	8.1		5.0	U
PBDE-066	5.1		5.2	U
PBDE-071	3.7	U	3.8	U
PBDE-099	300	JK	32	JK
PBDE-100	56	JK	8.7	JK
PBDE-138	42	UJK	260	U
PBDE-153	45	UJK	82	U
PBDE-154	52	JK	51	UJK
PBDE-183	96	UJK	100	UJK
PBDE-184	1700	U	2100	U
Total PBDEs	660		89	

U = The analyte was not detected at or above the reported result.
JK = The analyte was positively identified. Reported result is an estimate with unknown bias.
UJK = The analyte was not detected at or above the reported estimate with unknown bias.

Appendix L. Water Quality Criteria for Chemicals Analyzed

Table L-1. Water Quality Criteria for Chemicals Analyzed in the PBT Trends Study Using SPMDs (pg/L).

Chemical	Washington[a]				EPA (2006) Recommended Criteria[c]			
	Aquatic Life		Human Health (NTR)[b]		Aquatic Life		Human Health	
	Freshwater Acute	Freshwater Chronic	Water + Fish Consumption	Fish Consumption	Freshwater Acute	Freshwater Chronic	Water + Fish Consumption	Fish Consumption
p,p'-DDT	-	-	590	590	-	-	220	220
p,p'-DDE	-	-	590	590	-	-	220	220
p,p'-DDD	-	-	830	840	-	-	310	310
o,p'-DDT	-	-	-	-	-	-	-	-
o,p'-DDE	-	-	-	-	-	-	-	-
o,p'-DDD	-	-	-	-	-	-	-	-
DDT and metabolites[d]	1,100,000	1,000	-	-	1,100,000	1,000	-	-
DDMU[e]	-	-	-	-	-	-	-	-
Dieldrin	-	-	140	140	240,000	56,000	52	54
Aldrin	-	-	130	140	3,000,000	-	49	50
Dieldrin and aldrin[f]	2,500,000	1,900	-	-	-	-	-	-
Chlorpyrifos	83,000	41,000	-	-	83,000	41,000	-	-
Endosulfan[g]	220,000	56,000	-	-	220,000[h]	56,000[h]		
Endosulfan I (alpha)	-	-	930,000	2,000,000	220,000[h]	56,000[h]	62,000,000	89,000,000
Endosulfan-II (beta)	-	-	930,000	2,000,000	220,000[h]	56,000[h]	62,000,000	89,000,000
Endosulfan Sulfate	-	-	930,000	2,000,000	-	-	62,000,000	89,000,000
Hexachlorobenzene (HCB)	-	-	750	770	-	-	280	290
Pentachloroanisole (PCA)	-	-	-	-	-	-	-	-
Toxaphene	730,000	200	730	750	730,000	2,000	280	280
Total Chlordane[i]	2,400,000	4,300	570	590	2,400,000	4,300	800	810
Dacthal	-	-	-	-	-	-	-	-
Heptachlor	520,000	3,800	210	210	520,000	3,800	79	79

Chemical	Washington[a]				EPA (2006) Recommended Criteria[c]			
	Aquatic Life		Human Health (NTR)[b]		Aquatic Life		Human Health	
	Freshwater Acute	Freshwater Chronic	Water + Fish Consumption	Fish Consumption	Freshwater Acute	Freshwater Chronic	Water + Fish Consumption	Fish Consumption
Heptachlor Epoxide	-	-	100	110	520,000	3,800	39	39
alpha-Benzenehexachloride (a-BHC)	-	-	3,900	13,000	-	-	2,600	4,900
beta-Benzenehexachloride (b-BHC)	-	-	14,000	46,000	-	-	9,100	17,000
delta-Benzenehexachloride (d-BHC)	-	-	-	-	-	-	-	-
gamma - Benzenehexachloride (g-BHC) (Lindane)	2,000,000	80,000	19,000	63,000	950,000	-	980,000	1,800,000
Endrin	180,000	2,300	760,000	810,000	86,000	36,000	59,000	60,000
Endrin ketone	-	-	-	-	-	-	-	-
Endrin aldehyde	-	-	760,000	810,000	-	-	290,000	300,000
Mirex	-	-	-	-	-	1,000	-	-
p,p'-Methoxychlor	-	-	-	-	-	-	-	-
Total PCBs[j]	2,000,000	14,000	170	170	-	14,000	64	64
Total PBDEs[k]	-	-	-	-	-	-	-	-
PAHs	-	-	-	-	-	-	-	-

a - Water Quality Standards for Surface Waters of the State of Washington, Chapter 173-201A WAC (Ecology, 2006a).
b - EPA 1992 National Toxics Rule.
c - National Recommended Water Quality Criteria (EPA, 2006).
d - Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT as defined by Ecology, 2006b.
e - DDMU is a breakdown product of DDE.
f - Aldrin is metabolically converted to dieldrin. Therefore, the sum of the aldrin and dieldrin concentrations are compared with the dieldrin criteria.
g - Endosulfan is the sum of alpha and beta endosulfan.
h - Value derived from endosulfan and is appropriately applied to the sum of alpha- and beta-endosulfan (EPA, 2006).
i - Total chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane as defined by Ecology, 2006b.
j - Total PCBs is the sum of Aroclors or congeners.
k - Total PBDEs is the sum of the congeners.

Appendix M. Glossary, Acronyms, and Abbreviations

Glossary

Analyte: Water quality constituent being measured (parameter).

Anthropogenic: Human-caused.

Bioaccumulative pollutants: Pollutants that build up in the food chain.

Blank: A clean sample or sample of matrix prepared to contain none of the analyte of interest so as to measure artifacts in the measurement (sampling and analysis) process. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample.

Blank-correction: correcting the observed value (result from sample) using values of a blank as a specified part of a method procedure.

Blank-descriptions

- Field-trip: field and transport blank.
- Day0-dialysis: SPMD fabrication blank.
- FreshDay0: SPMD process blank.
- Dialysis No Spiked: unspiked SPMD process blank.
- Solvent-GPC: unspiked reagent blank; for PCBs only.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Congener: In chemistry, congeners are related chemicals. For example, polychlorinated biphenyls (PCBs) are a group of 209 related chemicals that are called congeners.

Exceeded criteria: Did not meet criteria.

Geometric mean: A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were calculated. This is helpful when analyzing bacteria concentrations, because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the nth root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Noise: The sum of all interference in a measurement which is independent of the data signal or true analyte result found in the sample.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Pathogen: Disease-causing microorganisms such as bacteria, protozoa, viruses.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Signal: The absolute amount of analyte in the ion source. In this report, the signal is the level of contaminant in the environment (analyte result from SPMD samples).

Spatial: How concentrations differ among various parts of the river.

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Temporal trends: Characterize trends over time.

Thermocline: A layer of water where there is an abrupt change in temperature that separates the warmer surface water from the colder deep water.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from exceeding water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): The suspended particulate matter in a water sample as retained by a filter.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards, and are not expected to improve within the next two years.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Acronyms and Abbreviations

BHP	benzene hexachloride (alpha-, beta-, gamma (gamma- also known as Lindane)
CFR	Code of Federal Regulations
CP	chlorinated pesticides
DDD	dichlorodiphenyldichloroethane (o,p’ and p,p’; 2,4’ and 4,4’)
DDE	dichlorodiphenyldichloroethylene (o,p’ and p,p’; 2,4’ and 4,4’)
DDMU	1-chloro-2, 2-bis (p-chlorophenyl) ethane (a breakdown product of DDE)
DDT	dichlorodiphenyltrichloroethane (o,p’ and p,p’; 2,4’ and 4,4’)
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
EST	Environmental Sampling Technologies
GC-ECD	gas chromatography – electron capture detection
GC-MS	gas chromatography – mass spectrometry
GPC	gel permeation chromatography
HPAH	high molecular PAH
K_{oc}	carbon-water partition coefficient
K_{ow}	octanol-water partition coefficient
LPAH	low molecular weight PAH
MEL	Manchester Environmental Laboratory
n	number
NPDES	(See Glossary above)
NTR	National Toxics Rule
PAH	polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic substance
PCB	polychlorinated biphenyl
PCDD/Fs	polychlorinated dibenzo-p-dioxins and -furans
PRC	permeability/performance reference compound
QA	quality assurance
QC	quality control
Rep	replicate
RM	river mile
RPD	relative percent difference
RSD	relative standard deviation
SOP	standard operating procedure
SPMD	semipermeable membrane device
T-DDT	total DDT (sum of detected metabolites)
TMDL	Total Maximum Daily Load (see Glossary above)
T-PAH	total PAH
T-PCB	total PCBs (sum of detected congeners)
TOC	total organic carbon
TSS	total suspended solids (see Glossary above)

USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resources Inventory Area
WSTMP	Washington State Toxics Monitoring Program
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
cm	centimeter
ft	feet
kcfs	1000 cubic feet per second
mg	milligrams
mg/L	milligrams per liter (parts per million)
mL	milliliters
ng	nanograms
pg/L	picograms per liter (parts per quadrillion)
ug/Kg	micrograms per kilogram (parts per billion)
um	micrometer
uS/cm	microsiemens per centimeter, a unit of conductivity